

**REMARKS**

Claims 1-2 and 15-17 were examined in the Office Action mailed January 3, 2008, while claims 18-49 stand withdrawn pursuant to election/restriction requirement. Claims 1-2 and 15-17 stand rejected under 35 U.S.C. § 103(a) as unpatentable over U.S. Patent No. 5,628,960 to Dr. Beer (“Beer ‘960”), and under § 103(a) as unpatentable over Beer ‘960 in view of U.S. Patent No. 5,826,129 to Hasebe, *et al.* (“Hasebe”).

In response to the Applicants’ October 30, 2007 amendments and remarks, it is maintained that it “is notoriously well known in the art to rinse a surface after it has been brushed to remove any loosened particles,” and that it would have been obvious to modify Beer ‘960 to rinse the surface after brushing. January 3, 2008 Office Action at 2.

In addition, in the Response to Arguments section it is maintained that the while the present Specification teaches the use of an anionic wetting agent, it is not clear that one of skill in the art would be able to pick the sodium alkyl sulfonate discussed in Dr. Beer declaration from the “hundreds of thousands” of anionic wetting agents available, and that in any event sodium alkyl sulfonate is not recited in the claims. *Id.* at 3.

Finally, it is requested that the Applicants submit corroborating evidence in support of the statement that one of ordinary skill in the art would have recognized “casting dope” as equating to the claimed “process inversion.” *Id.*

The following remarks and attached supporting documents respond to these issues.

**1, By Focusing Narrowly On the Brushing Feature, The Novelty Of The Present Invention As A Whole Is Missed.** As a threshold matter, the Applicants wish to reiterate that the present invention is not the mere brushing and rinsing of a membrane after its initial formation, but rather reflect the inventors' fundamentally approach to producing the membranes – *an approach which is literally the reverse of the prior art approach.*

As discussed in the present Specification and in the Applicants' earlier responses, previously membranes were formed from very expensive, highly-purified membrane feedstock materials, and allowed to dry without any further cleaning – thus a “dust-free” finish membranes was obtained at the “*front end*” of the process by the use of these highly-purified liquids.

In contrast, the inventors took exactly the opposite tack, developing a membrane formation process which shifted dust elimination to the “*back end*” of the membrane formation process – directly contrary to the common view in the art that these easily damaged membranes could *not* be easily and reliably mechanically cleaned after formation (in part because prior attempts at post-membrane formation dust removal were conducted on membranes which could not withstand the mechanical cleaning stresses). In the present invention, as part of taking a completely different approach, the inventors developed a different approach to post-formation cleaning, discovering that dust removal “*prior to drying* the resulting feedstock membrane” (claim 1) allowed mechanical cleaning without significant membrane damage. Thus, by fundamentally changing the approach to membrane formation, the inventors were able to

eliminate the need for expensive, high-purity feedstock materials.

Accordingly, while the pending Office Action focuses on whether mechanical cleaning was or was not obvious, the Applicants respectfully submit that the invention does not lay solely in the particular approach to back end cleaning, *but in the shift from the long-established use of highly refined feedstocks in the front end of the process to the use of lower purity feedstocks in combination with a new approach to back end dust removal (i.e., the cleaning of the still wet newly formed membrane).*

**2. The Issues In The Pending Office Action.** Turning to the specific issues identified in the January 3, 2008 Office Action, as a first matter the Applicants note that Beer '960 contains nothing which teaches or suggests the Applicants' novel approach of conducting the cleaning step while the newly-formed membrane is still *partially wet* (per claim 1, "prior to drying"). In other words, Beer '960 not only fails to teach the recited mechanical brushing while rinsing, it also fails to teach or suggest *the specific stage at which this process step is to be carried out.*<sup>1</sup> As to the Hasebe reference, the Applicants respectfully submit that one of ordinary skill in the art would not have considered a water jet cleaning process used to clean hard, rigid semiconductor wafer surfaces when developing a process for removing "dust" from these extraordinarily delicate

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<sup>1</sup> While the Applicants recognize that the examination of applications in corresponding foreign cases are not binding in a U.S. case, in support of the Applicants' position that the claimed process *as a whole* is a new, unobvious departure from the prior art the Applicants note the recognition of the claimed subject matter as novel by the Examiner's peers in Germany. Not only were broader versions of the U.S. claims allowed in the corresponding German application, but in a following opposition proceeding, the essentially unamended claims were maintained.

membranes.<sup>2</sup>

With respect to the Examiner's remarks regarding anionic wetting agents and provision of additional supporting information, the Applicant first notes that in the Response to Arguments it is stated that the Applicants "would equate the taught "anionic wetting agent" with the "sodium alkyl sulfonate" referenced in the 9/28/07 37 CFR 1.132 Declaration." January 3, 2008 Office Action at 3. This statement then provides the springboard for the assertion that those of ordinary skill in the art "would have no ability to pick" sodium alkyl sulfonate from the "hundreds of thousands" of known anionic agents. The Applicants respectfully submit that these statements fundamentally misstate the Applicants' comments, and create an issue where none exists.

The Applicants *did not state that sodium alkyl sulfonate is the anionic wetting agent* recited in the claims. Rather, in response to the Examiner's earlier request for evidence regarding the superior results of the inventive membrane formation process, Dr. Beer in his declaration identified how the test membranes were prepared, and identified sodium alkyl sulfonate as the particular anionic wetting agent *that he used* in the testing. Dr. Beer *did not* state that sodium alkyl sulfonate is the *only* anionic wetting agent that is suitable for use with the claimed membrane formation process. Thus, the suggestion in the pending

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<sup>2</sup> The Applicants further note that this is not the usual case of attempting to develop an *improved* process (here, an improved cleaning process), but instead the unusual case of developing *an entirely new approach to membrane production* (there not having been a post-formation cleaning approach in the prior art, because it was not believed the membranes could be cleaned after formation).

Office Action that the Applicants “equate” sodium alkyl sulfonate to the claimed anionic wetting agent – *to the exclusion of other such agents* – is incorrect.

In view of these facts, the Applicants submit the current thrust of the January 3, 2008 Response to Arguments is misdirected. Essentially, the argument is that the Applicants state that sodium alkyl sulfonate is the claimed anionic wetting agent, but that because sodium alkyl sulfonate is not specifically mentioned in the Specification or the claims, one of ordinary skill in the art would not be able to pick the sodium alkyl sulfonate from the “hundreds of thousands” of anionic wetting agents available. The Applicants have never asserted that sodium alkyl sulfonate is *the* anionic wetting agent, and there is no reason to now limit the claims to a particular anionic wetting agent.

Further, unlike the case in which there may be some question as to whether alternative materials may behave in a different manner with respect to their *chemical* effects, in the present case, the anionic wetting agent’s uses is solely for its *physical* effects – as the Specification makes clear, the anionic wetting agent is introduced as a surfactant (or “tenside”) whose polar and non-polar sites perform a singular physical function. Thus, one of ordinary skill in *this* art would not be “at sea” trying to decide which of “hundreds of thousands” of anionic agents to use, as they all share the same *physical* properties of a surfactant. Indeed, when the Specification and claims are read from the perspective of one of ordinary skill in the art (as required by the MPEP), it should be beyond question that one of ordinary skill would recognize any of a number of anionic wetting agents – including sodium alkyl sulfonate – as

commonly used as surfactants/wetting agents in this particular art. In response to the request for evidence, the Applicants have attached for example the Annex I Chemical Abstracts excerpt identifying appropriate anionic wetting agents (sodium alkyl sulfonate being one of the included agents). In addition, attached as Annex II is a portion of the Römpps Chemical Encyclopedia, 7<sup>th</sup> Ed., dealing with tensides such as sodium alkyl sulfonate (German language), and a similar description of surfactants and tensides as wetting agents from as common a source as Wikipedia (<http://en.wikipedia.org/wiki/Tenside>). For specific tensides, the Examiner's attention is drawn to the table at page 3495, wherein a number of commonly used tensides, such as sodium alkyl sulfonates, are identified.

In view of the foregoing, the Applicants respectfully submit that there should be no issue arising from Dr. Beer's identification of the specific anionic wetting agent he used in his testing, and that in view of the knowledge one of ordinary skill would possess of the anionic wetting agents available and commonly used in this art, the present Specification and claims are perfectly satisfactory under 35 U.S.C. § 112.

Finally, with respect to the Examiner's inquiry regarding the relationship between casting solutions and phase inversion, attached as Annex III is Chapter 7 of Synthetic Polymeric Membranes, 2<sup>nd</sup> Ed., 1985, Robert E. Kesting. This reference describes the well known mechanism of phase inversion in which a solution undergoes a gelation in the membrane formation process as the membrane is cast. *See, e.g.*, page 237-238 and Fig. 7.1 (describing the basics of gelation process in membrane casting). As noted at page 252 of this reference,

the formation of membranes in a phase inversion process is referred to as “casting” of the “casting solution” (the gelling solution also being referred to as the casting dope). The Applicants respectfully submit that there should be no question that those of ordinary skill in the art immediately associate “casting” with phase inversion.

### **CONCLUSION**

The Applicants respectfully submit that in view of the foregoing remarks and attached supporting Annexes, claim 1 and its dependent claims 2 and 15-17 are in condition for allowance. Early and favorable consideration and issuance of a Notice of Allowance for these claims is respectfully requested.


If there are any questions regarding this Preliminary Amendment or the application in general, a telephone call to the undersigned would be appreciated since this should expedite the prosecution of the application for all concerned.

If necessary to effect a timely response, this paper should be considered as a petition for an Extension of Time sufficient to effect a timely response, and please charge any deficiency in fees or credit any overpayments to Deposit

Account No. 05-1323 (Docket # 103655.50685US).

Respectfully submitted,

March 28, 2008

A handwritten signature in black ink, appearing to read "J.D. Evans", written over a horizontal line.

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# **ANNEX I**

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AN 145:498255 CA Full-text

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TI Preparation method of colloid composition containing iron oxide nanoparticles and colloid solution prepared by the method  
IN Baek, Seong Sik; Jun, Yong Ju; Kim, Hyeon Cheol; Lee, Byeong Du; Lee, Mun

Ho

PA Postech Foundation, S. Korea

SO Repub. Korean Kongkae Taeho Kongbo, No pp. given  
CODEN: KRXXA7

DT Patent

LA Korean

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	KR 2004078853	A	20040913	KR 2003-13745	20030305
PRAI	KR 2003-13745		20030305		

AB A method for preparing a colloid solution containing iron oxide nanoparticles and a colloid solution prepared by the method are provided, to obtain a colloid solution containing iron oxide nanoparticles which is transparent, stable and highly dispersive and is free from precipitation. The method comprises the steps of dissolving a surfactant in an organic solvent to prepare a surfactant solution; mixing an iron salt aqueous solution and the surfactant solution homogeneously to prepare an emulsion; mixing a basic solution and the surfactant solution homogeneously to prepare a basic mixture solution; and mixing the emulsion and the basic mixture solution. Preferably the surfactant is at least one **anionic surfactant selected from the group consisting of** sodium dodecyl sulfate, sodium bis(2-ethylhexyl)sulfosuccinate, dodecyl benzenesulfonic acid, sodium dioctyl sulfosuccinate, sodium alkyl phenol ether sulfonate and **sodium alkyl sulfonate**; the iron salt is at least one selected from the group consisting of iron sulfate, FeCl<sub>2</sub>, FeCl<sub>3</sub>, iron nitrate, pentacarbonyl iron, iron acetate, iron oxalate and iron ammonium sulfate; and the basic material of the basic solution is at least one selected from the group consisting of NaOH, KOH, LiOH, tetra-Me ammonia, ammonia and sodium carbonate.

# **ANNEX II**

# Römpps Chemie-Lexikon

Völlig neubearbeitete und erweiterte  
siebte Auflage des von  
Professor Dr. Hermann Römpp  
begründeten und in sechster Auflage von  
Dipl.-Chem. Dr. Erhard Ühle  
fortgeführten Chemie-Lexikons



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Stuttgart

Schutzumschlag und Einband von Edgar Dambacher  
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**CIP-Kurztitelaufnahme der Deutschen Bibliothek**

**Neumüller, Otto-Albrecht**

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ISBN 3-440-03850-5

NE: Römpp, Hermann: Chemie-Lexikon

Bd. 6. T—Z. Formelregister.

Dictionary (English/German). Dictionnaire (Français/Allemand).

Völlig Neubearb. u. erw. 7. Aufl.

d. von Hermann Römpp begr. u. in

6. Aufl. von Erhard Uhlein fortgef. Chemie-

Lexikons, 41.—50. Tsd. — 1977.

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eine 100%ige Tochterges. von Hercules. *Produktion*: Anorg. u. org. Pigmente. *Vertr.* in der BRD: Hercules GmbH, 2050 Hamburg 80.

**Tenifer** ®. Wz. für Salze u. für ein Verf. zur \*Nitrierhärtung von Stählen für Kurbel- u. Nockenwellen, Zahnräder, Teile von Wasserpumpen, Zylinderköpfe für Dieselmotoren, Ventile, Werkzeuge u. a. Kleinteile usw. Die Werkstücke werden in eine 570° heiße Schmelze, bestehend aus Cyanid- u. Cyanatsalzen, gebracht. Dabei bildet sich Eisennitrid in der Metalloberfläche, zur Chemie bei der T.-Behandlung s. Beyer et al. (CAV 1973, Nr. 11, S. 69—75). Die Behandlungsdauer beträgt je nach Verwendungszweck 30—180 Minuten.

B.: Degussa.

**Tenite** ®. Wz. von Eastman für Spritzguß- od. Extrusionsmassen aus Celluloseacetat, -acetobutyrat u. -acetopropionat sowie Polypropylen. T. PTMT ist ein Polytetramethylenterephthalat-Thermoplast zum Einsatz im Apparatebau u. in der Kraftfahrzeug- u. Maschinenind., T. PCDT ein Copolymeres aus 1,4-Cyclohexandimethanol u. Terephthal- u. Isophthalsäure zur Verw. als Pulverlack.

B.: Krahn.

**Tenlo**. Pigmentmahlhilfsstoffe u. Dispergiermittel auf der Basis einer Mischung nichtionogener oberflächenakt. Substanzen, bes. geeignet für Eisenpigmente.

B.: Nopco.

**Tenn** ®. Bleichendes Putz- u. Scheuermittel mit org. Chlorträger u. Quarzmehl als Abrasivkomponente sowie Tensiden u. Polyphosphaten zur Emulgierung fetthaltigen Schmutzes. Wegen seiner mikrobiziden Wrkg. ist T. auch zur Reinigung von Ausgüssen u. Toiletten verwendbar.

B.: Henkel.

**Tennant**, Smithson (1761—1815), Prof. Chemie Univ. Cambridge. *Arbeitsgebiete*: Diamanten, Einw. von KNO<sub>3</sub> auf Au u. Pt, Entdeckung von Os u. Ir im Rohplatin, Darst. von Weinsäure (aus Weinstein), Citronensäure (aus Zitronensaft), Oxalsäure u. dgl.

*Lit.*: Nature 192 (1961) 1224—1226; Weeks u. Leicester, The Discovery of the Elements, Easton: J. Chem. Educ. 1968, S. 414—418.

**Tennantit**, 3 Cu<sub>2</sub>S·As<sub>2</sub>S<sub>3</sub>. Graues Kupfererz aus Colorado, Wyoming, Montana. Name nach S. \*Tennant. — E tennantite

*Lit.*: Doelter 4/1: 184—188; Ramdohr-Strunz, S. 418—419; Ullmann 11: 132.

**Tenneco**. Kurzbez. für die Tenneco Chemicals Inc., Park 80 Plaza West-1, Saddle Brook, N. J. 07662 (USA). Die Firma ist eine Tochterges. der Tenneco International Inc. (Umsatz 1974: 5 Mrd. \$), die seit 1975 zu ca. 50% an Albright & Wilson beteiligt ist. *Daten* (1974): 5800 Beschäftigte, 366 Mio. \$ Umsatz. *Produktion*: Org.

Chemikalien, Petrochemikalien, Kunststoffe, Lecke, Farben, Druckfarben, Naval Stores, Wasmacher.

*Lit.*: Weber, Lichtbogen 24 (1975) Nr. 2, S. 4—  
**Tenopur** ®. Wz. für ein Verf. zur Herst. Grauguß mit bes. Zähigkeitseig. mit Hilfe bes. Vorleg., Sonderimpfmitteln u. Gießereihilfsstoffen.

B.: Metallgesellschaft.

**Tenoran** ®. Wz. von Ciba-Geigy für ein Hezid, auf der Basis von 3-[4-(4-Chlorphenylphenyl)-1,1-dimethylharnstoff (Chloroxuron) Verw. in Gemüse-, Obst-, Zier- u. Sojakulturen. B.: Ciba-Geigy; Philips-Duphar; Riedel.

**Tenorit**. Mineral aus Kupfer(II)-oxid, Härte 3—4, D. 6, Verwitterungsprod. and Cu-Erze. *Vork.*: Auf Vesuvlaven, bei Walds (Bayern), in Tennessee, verbreitet in Katal am Lake Superior usw. Name von Prof. Ten Neapel. — E tenoriten

*Lit.*: Doelter 3/2: 98—105; Gmelin, Syst.-Nr. 60, Tl. A, 1955, S. 172; Ramdohr-Strunz, S. 483; mann 11: 132, 244.

**Tenosin** ®. Tropfen mit Tyraminhydrochlorid Histamindihydrochlorid gegen gynäkolog. tungen.

B.: Bayer.

**Tenox** ®. Wz. von Eastman für Antioxidant z. B. T. BHA u. T. BHT.

B.: Krahn.

**Tensammetrie** s. \*Voltammetrie. — E tensammetry

**Tenside**. Von Götte (Fette, Seifen, Anstrichmittel 62 (1960) 789—790) eingeführte u. von tendere = spannen abgeleitete Sammelbez. *grenzflächenaktive Verbindungen*, die früher z. T. aus dem engl. Sprachgebrauch übernommen u. z. T. in abweichendem Sinn verstanden. Benennungen wie *Syndets*, *Surfactants*, *Sapto waschaktive Stoffe* (WAS) u. dgl. verdrängt. Die Bez. Tenside ist nicht gleichbedeutend mit der Bez. \*Detergentien, denn letztere umfassen auch \*Waschmittel, die u. a. T. enthalten. Näheres zur Terminologie s. im Vokabularium von Tensiden Paris: Comité International des Dérivés Tensidactifs 1972, u. eine T.-Klassifikation findet man in Tenside Detergents 11 (1974) 185—194. DIN 53 900 (Juli 1972) definiert ein Tensid als eine „chem. Verb., die, in einer Fl. gelöst od. dispergiert, an einer Grenzfläche bevorzugt adsorbierbar wird; dadurch wird eine Anzahl von prakt. bedeutungsvollen physikal.-chem. od. chem. Eff. hervorgerufen. Die Molekel der Verb. besitzen wenigstens eine Gruppe mit Affinität zu Substanzen starker Polarität — wodurch im allg. die Löslichkeit in Wasser verursacht wird — u. eine weitere Gruppe mit geringer Affinität zu Wasser. Die in der Praxis gebrauchten Prod. sind im allg. Mischungen solcher Verbindungen.“ T. sind also

\*grenzflächenaktive Stoffe, deren Mol. einen \*lipophilen (\*hydrophoben, d. h. wasserabweisenden = fettfreundlichen) org. Rest — meist einen Kohlenwasserstoffrest mit Alkyl- u./od. Arylkomponten, in den Abb. durch

Stäbchen symbolisiert — u. eine \*hydrophile (\*lipophobe, d. h. wasserfreundliche = fettabweisende) Gruppe aufweisen, die in den Abb. durch einen Kreis symbolisiert ist. Bes. hydrophob ist der Perfluoralkylrest, was die speziellen Anwendungen der sog. *Fluortenside* bedingt, s. \*perfluorierte Verbindungen.

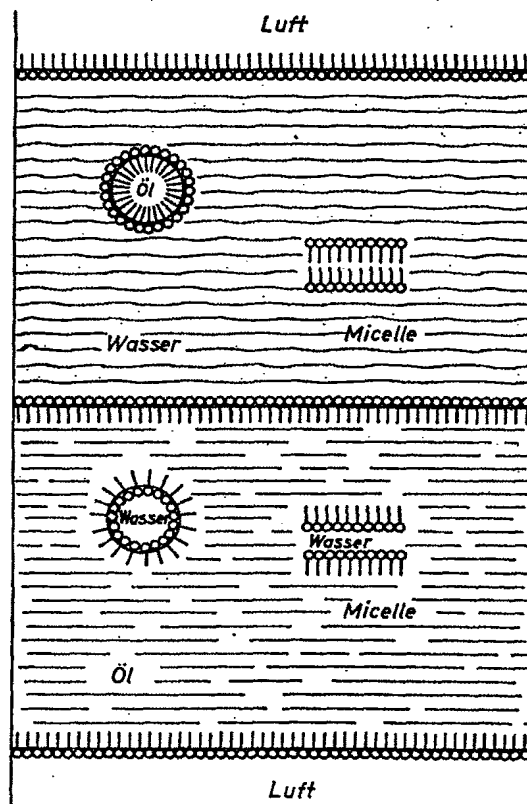
Durch ihren *amphiphilen* Aufbau (s. \*amphiphile Verbindungen) reichern sich die T.-Mol. in der Oberfläche ihrer Lsg. u. an fl. u. festen \*Grenzflächen in bestimmter Weise an, durch die zahlrei-

che physikal.-chem. Erscheinungen — insbes. die Erniedrigung der \*Grenz- od. Oberflächenspannung — ausgelöst werden, die u. a. die Wrkg. der T. beim Waschen, Benetzen, Emulgieren, Reinigen u. Dispergieren bedingen. Die Funktion der T. kann man sich anhand der stark vereinfachten Abb. verdeutlichen, die sich auch zur Veranschaulichung der \*Solubilisation heranziehen läßt, wenn man sich vorstellt, daß im oberen Teil der Abb. der Micelle ein wasserunlös. Mol. (Kohlenwasserstoff, Lipoid etc.) eingelagert ist. Die T.-Mol. wirken hier als \*Lösungsvermittler. Diese Solubilisation spielt ebenso wie die verwandte \*Hydrotropie (Rath, Tenside 2 (1965) 1-6) bei \*Emulsionen eine große Rolle, s. a. \*HLB-System u. Schwuger (Chemiker-Ztg. 96 (1972) 248-253 u. Kolloid-Z. Z. Polym. 250 (1972) 703-710). Die Bldg. von \*Micellen (*Assoziationskolloide*, s. \*Kolloidchemie, S. 1825) wird auch dafür verantwortlich gemacht, daß sich bei wss. T.-Lsg. Eig. wie Oberflächen-(\*Grenzflächen-)Spannung, elektr. Leitfähigkeit, Viskosität, osmot. Druck etc. nicht proportional der Konz. ändern; Näheres s. bei Shedlovsky (Ind. Eng. Chem. 60 (1968) Nr. 10, S. 47-52), Chwala u. Anger (Endeavour 30 (1971) 97 bis 100), Kurzendörfer u. Lange (Fortschrittsber. Kolloide Polym. 55 (1971) 124-130), Lange u.

Abb. (rechts): Schematische Darstellung der Verteilung von Tensid-Molekeln in Wasser bzw. Öl u. gegenüber Luft sowie der Bildung von Micellen

Hydrophob	Hydrophil	Gegenion	Tensid-Typ	Beispiele
Alkyl-, Alkylaryl-	-COO <sup>⊖</sup>	Na <sup>⊕</sup>	Anionaktiv	*Seifen, Carboxylate
Alkyl-, Alkylaryl-	-SO <sub>3</sub> <sup>⊖</sup>	Na <sup>⊕</sup>	Anionaktiv	*Sulfonate
Alkyl-, Alkylaryl-	-O-SO <sub>3</sub> <sup>⊖</sup>	Na <sup>⊕</sup>	Anionaktiv	*Sulfate
Alkyl-, Alkylaryl-	-NH <sub>2</sub> ·H <sup>⊕</sup>	Cl <sup>⊖</sup>	Kationaktiv	Aminsalze
Alkyl-, Alkylaryl-	-N <sup>⊕</sup> R <sub>3</sub>	Cl <sup>⊖</sup>	Kationaktiv	*Invertseifen, *quartäre Ammoniumverbindungen
Alkyl-, Alkylaryl-	-(CH <sub>2</sub> -CH <sub>2</sub> O) <sub>n</sub> -H		Nichtionogen	Äthoxylate
Alkyl-, Alkylaryl-	-(CH <sub>2</sub> -CH <sub>2</sub> O) <sub>n</sub> -H		Nichtionogen	Äthoxylate
Alkyl-, Alkylaryl-	-(CH <sub>2</sub> -CH <sub>2</sub> O) <sub>n</sub> -H		Nichtionogen	Äthoxylate
Alkyl-, Alkylaryl-	-(CH <sub>2</sub> -CH <sub>2</sub> O) <sub>n</sub> -H		Nichtionogen	Äthoxylate
Alkyl-, Alkylaryl-	Zuckerrest		Nichtionogen	*Zuckerester
Alkyl-, Alkylaryl-	-N→O		Nichtionogen	*Aminoxide
Alkyl-, Alkylaryl-	-CH-COO <sup>⊖</sup>		Amphoter	Betaine
Alkyl-, Alkylaryl-	-CH-SO <sub>3</sub> <sup>⊖</sup>		Amphoter	*Sulfobetaine

Tab.: Einteilung der Tenside mit Beispielen



Beck (Kolloid-Z. Z. Polym. 251 (1973) 424 bis 431), Hoffmann (Nachr. Chem. Techn. 24 (1976) 444 f.) u. Wagner (Wasser-Kal. 9 (1975) 164 bis 167). Über den Einfl. der Micellenbildg. bei der Katalyse von Hydrolysevorgängen durch T. berichten Cordes u. Boll (Chem. Rev. 74 (1974) 581–603, bes. S. 599–602), u. allg. über Reaktionskinetik in micellbildenden T. s. Progr. Bioorg. Chem. 2 (1973) 1 ff.

Man unterscheidet bei den T. – vgl. die Tab. u. die Einzelstichwörter – *\*Aniontenside* wie Seifen, Alkansulfonate, Olefinsulfonate, Estersulfonate, Alkylarylsulfonate, insbes. Alkylbenzolsulfonate vom Typ des Dodecylbenzolsulfonats u. Alkyl-naphthalinsulfonate, Alkylsulfate, Äthersulfate, Fettalkohol(äther)sulfate; *\*Kationtenside* wie geradkettige u. cycl. Ammoniumverb., die früher Invertseifen genannten Verb., Benzalkoniumchloride u. a. quartäre Ammoniumsalze, Aminsäuren, Pyridiniumsalze; *\*Nichtionogene Tenside* wie Polyäther, insbes. Alkylphenolpolyglykoläther u. a. Prod. der *\*Äthoxylierung* von Fettsäuren, Fettsäureamiden, Fettaminen u. Fettalkoholen, ferner Aminoxide (Kirk-Othmer S: 44–46) u. Fettsäureester von Polyalkoholen, insbes. Zuckerester; *\*Amphotenside* (ampholyt. T.), die als *\*Zwitterionen* anionakt. u. kationakt. hydrophile Gruppen in sich vereinigen, wie Glycinderiv. mit *\*Betain-Struktur* (insbes. *\*Tegobetaine* u. *\*Miranol-* bzw. *\*Steinapon-Typen*) sowie Sulfobetaine (Hüttinger, Goldschmidt informiert 1975, Nr. 1, S. 42–46 u. Hein, Parfümerie Kosmetik 56 (1975) 339–344). Von den 300 000 t T., die 1971 in der BRD verwendet wurden (Stache, Tenside Detergents 10 (1973) 78 ff.), entfielen ca. 73% auf anionakt., ca. 22% auf nichtionogene u. ca. 5% auf kationakt. T., während Amphotenside nur einen verschwindend kleinen Beitrag leisteten. Bes. Bedeutung wird der Weiterentw. der nichtionogenen T. zugemessen. Ferner stellt man Vers. an, den Anteil der in Waschmitteln (*\*Detergentien*) noch benötigten Phosphate dadurch zu mindern, daß man deren Builder-Funktion (s. *\*Waschmittel*) von komplexbildenden u. kalkdispergierenden T. übernehmen läßt, die außer einer Sulfat- od. Sulfonatgruppierung benachbarte funktionelle Gruppen wie Sulfonamido-, Carbonyl-, Ester- od. Ammonio-gruppierungen tragen (Linfield, Tenside Detergents 11 (1974) 260). Im allg. wirkt sich der Einbau einer zweiten hydrophilen Gruppe in T. auf die Gesamteig. nicht günstig aus (Götte, Fette, Seifen, Anstrichmittel 71 (1969) 219–223). Auch Rohstoffprobleme spielen bei der Entw. moderner T. eine Rolle, wie die Herst. von T. aus Maisstärke bzw. tierischen od. pflanzlichen Proteinen zeigt (Throckmorton et al. bzw. Sokol, J. Am. Oil Chem. Soc. 51 (1974) 486 bzw. 52 (1975) 101).

Allg. Gesichtspunkte zur Herst. der T. s. Hofstetter (Dtsch. Färber-Kal. 75 (1971) 588–626), Fell (Tenside Detergents 12 (1975) 3) u. in Winnacker-Küchler (3.) 4: 422–506.

Zur qual. u. quant. Analyse der T. sind reiche Verf. entwickelt worden, die auf Fällung od. Titrationsbasis mit Photometrie od. Lösungsmessung arbeiten. Aniontenside beispielsweise werden durch p-Toluidin od. mit Bariumchlorid gefällt, mit Kationtensiden titriert (Epton-Titration) od. nach der Methylenblau-Methode von Longwell u. Maniece (als MBAS = methylenblau-akt. Substanz) bestimmt, Kationtenside ebenfalls nach Epton titriert od. mit Reingold-Salz bzw. Phosphorwolframsäure gefällt. Ebenso sind für die Analyse nichtionogener (*\*Wickham-Methode*) u. ampholyt. T. Spezialmeth. erarbeitet worden. Näheres zur T.-Analytik s. bei Buere, Großmann (Lit., dort S. 123–143), bei Schöberl et al. (Chemiker-Ztg. 99 (1975) 301–307), in Waschmittelchemie (Lit., S. 205–220) u. in Chem. Produkt. 3 (1974) Nr. 6, S. 44–45. Die Fällungsgruppe „Wasserchemie“ der *\*GDCh* hat entsprechende Analysenvorschriften (Deutsche Einheitsverfahrens. Lit.) erlassen wie die *\*Deutsche Gesellschaft für Fettwissenschaft*, u. auch die *\*Detergentien-Kommission* vom 1. 12. 1962 (BGBl. I S. 698–700) u. das bis 1975 gültige Detergentien-Gesetz vom 12. 9. 1961 (BGBl. I S. 1653) enth. Anweisungen für die T.-Analyse. Ebenso wichtig wie die Analysenmeth. sind die anwendungstechn. Verfahrensmeth. zur Ermittlung der Gebrauchswerte: der Hartwasserbeständigkeit, von Trübungspunkt, Viskosität, Gelierungstemp., Lagerungsverh., u. bes. aber um die Best. der wichtigsten T.-Eigenschaften: Wasch-, Netz- u. Schaumvermögen. Beschreibungen dieser Meth. liegen vor in DIN 53 901–53 919 u. a. DIN- u. ISO-Normen, in Waschmittelchemie (Lit.) u. in Waschmittelchemie (Lit.) 102 (1976) 6 ff., 35 ff., 111 ff., 122 ff. u. 162 ff.

Diesen Analysenthemen hat sich seit dem Aufkommen von Begriffen wie *\*Ökologie* u. *\*Umweltschutz* in den 50er Jahren die Best. der *\*biologischen Abbaubarkeit* hinzugesellt, seit man nämlich feststellen mußte, daß viele der seit langem verwendeten T. zu Schaumbelästigungen in Seen u. Flüssen führten u. auch die Frage der Toxizität für Fische u. a. Bewohner des Ökosystems Wasser in Betracht zu ziehen war, vgl. Berth et al. (Tenside Detergents 9 (1972) 20 bis 267). Die Ursache war in der Tatsache zu suchen, daß der *\*biologische Abbau* der zunächst eingesetzten, umgangssprachlich auch als *harte* bezeichneten Verb. vom Typ des *\*Tetrapropylbenzolsulfonats* wegen der Kettenverzweigung im Alkylteil nicht funktionieren konnte – Mikroorganismen „knabbern“ Kettenmol. im allg. in C<sub>2</sub>-Einheiten ab – u. die T. aus dem *\*Abwasser*



über die Kläranlagen nahezu unversehrt in die offenen Gewässer gelangten, aus denen die öffentliche Wasserversorgung gespeist wird. Näheres zur Prüfung der biolog. Abbaubarkeit s. bei Fischer (Tenside Detergents 8 (1971) 177–188 u. Vom Wasser 40 (1973) 305–334) u. Wickbold (Tenside Detergents 11 (1974) 137–144). Heute sind die Schaumberge auf den Flüssen weitestgehend verschwunden, weil die neuen, manchmal auch als weiche T. bezeichneten Verb. mit linearen (unverzweigten) Seitenketten zu mehr als 80% (Forderung des \*Detergentengesetzes von 1961) abbaubar sind. Im neuen Gesetz vom 20. 8. 1975 (BGBl. I S. 2255–2257) u. in der zugehörigen Durchführungsverordnung (Waschmittel-VO) soll die Abbaurate von mindestens 80% auch für nichtionische Tenside gelten, vgl. Fischer (Tenside Detergents 12 (1975) 53 bis 64). Die Best. der biolog. Abbaubarkeit der T. steht in engem Zusammenhang mit der Ermittlung anderer Kenndaten von \*Wasser u. \*Abwasser, insbes. mit der des biochemischen u. chemischen \*Sauerstoffbedarfs (Näheres s. dort u. vgl. \*BSB) u. des Kohlenstoffgeh. (s. \*TOC). Allgemeinverständlich umfaßt die T.-Analyse auch die Prüfung auf humantoxische u. dermatolog. Eig., vgl. Götte (Tenside 4 (1967) 209–217), Tronitz (Goldschmidt informiert 1975, Nr. 1, S. 36 bis 41), Gloxhuber (Arch. Toxicol. 32 (1974) 267–270) u. Swisher (Lit.).

Wichtigste T. hauptsächlich als Bestandteil von \*Waschmitteln, in denen T. 10–15% ausmachen (Lehmann, Chemie uns. Zeit 7 (1973) 82–89), u. Reinigungsmitteln, ferner als \*Netzmittel (Lehmann, Dtsch. Färber-Kal. 75 (1971) 640 bis 658), \*Schaumbildner, \*Reinigungsverstärker (\*kationaktive), \*Textilhilfsmittel, \*Antifouling, Emulgatoren, als Zusatz zu Lötlutten, \*Schutzbädern, galvan. Bädern, Schneid- u. \*Polieren, Flotationschemikalien, Korrosions-Schutzmitteln, Bitumen, Schädlingsbekämpfungsmitteln, Farben usw., zur Staubbindung in Bergbau, zur Herst. gleichmäßiger \*Emulsionen in \*Margarine-, Backwaren- u. Schokoladenind., \*Papier-, Leder-, Klebstoff-, Gummi- u. Kunststoffind., zur Lösungsvermittlung in der \*Kosmetik u. Arzneimittellind. (Thoma, Parfümerie Kosmetik 57 (1976) 63–68), als Desinfektionsmittel usw., vgl. a. Chwala u. Anger (oben) u. den Bericht über den 6. Internat. Kongreß für grenzflächenakt. Stoffe (Zürich 1972) in Chem. Rdsch. 25 (1972) 1061–1091. Im Jahre 1971 in der BRD verbrauchten 100 000 t T. entfielen 34,4% auf \*Seifen, 35,5% auf Haushaltswasch- u. -reinigungsmittel, 5,9% auf die techn. u. insbes. chem. Ind., 4,1% auf \*Kosmetik, 4,0% auf die Textilind., 3,6% auf gewerbliche Wäscherei- u. Reinigungsbetriebe u.

2,5% auf die Metallindustrie. — E surface active agents, surfactants — F agents tensio-actifs, agents de surface, surfactifs

**Tensid**  
**3497**

Lit.: Book of ASTM Standards, Part 30: Soap, Engine Coolants, ..., Philadelphia: ASTM (jährlich); Buuren u. Grossmann, Grenzflächenaktive Substanzen, Weinheim: Verl. Chemie 1971; Carrière, Lexicon of Detergents, Cosmetics and Toiletries, Amsterdam: Elsevier 1966; Chemie, physikalische Chemie u. Anwendungstechnik der grenzflächenaktiven Stoffe (3 Bde.), München: Hanser 1973; Chemistry, Physics and Application of Surface Active Substances (3 Bde.), London: Gordon and Breach 1967; Colson, Les surfactifs en cosmétologie, Paris: Eyrolles 1974; Davidsohn u. Milwidsky, Synthetic Detergents, London: Hill 1972; Deutsche Einheitsmethoden zur Untersuchung von Fetten, Fettprodukten u. verwandten Stoffen (DGF-Einheitsmethoden), Lief. 9, Abt. H: Organische grenzflächenaktive Stoffe (Tenside), Stuttgart: Wiss. Verlagsges. 1965; Deutsche Einheitsverfahren zur Wasser-, Abwasser- u. Schlammuntersuchung, Weinheim: Verl. Chemie 1960–1971; Elworthy et al., Solubilization by Surface-Active Agents and its Applications in Chemistry and the Biological Sciences, London: Chapman and Hall 1968; Fendler u. Fendler, Catalysis in Micellar and Macromolecular Systems, New York: Academic Press 1975; Gawalek, Tenside, Berlin: Akademie-Verl. 1976; Götzelmann, Probleme nichtionogener Tenside beim Einsatz von Ionenaustauschern für die Wasserrückgewinnung in der metallverarbeitenden Industrie, München: Oldenbourg 1972; Grenzflächenaktive Stoffe in der Waschmittel- u. Textilhilfsmittel-Industrie, Berlin: Akademie-Verl. 1963; Hummel, Analyse der Tenside (2 Bde.), München: Hanser 1962 (engl. bei Wiley 1964); 4. Internationale Tagung über grenzflächenaktive Stoffe, Berlin: Akademie-Verl. 1977; Jungermann, Cationic Surfactants, New York: Dekker 1970; Kirk-Othmer 6: 853–895, 19: 507–593; Kölbel u. Kurzendörfer, Fortschr. Chem. Forsch. 12 (1969) 252 bis 348; Liebmann, Detergentien u. Öle im Wasser u. Abwasser. Möglichkeiten ihrer Zurückhaltung u. Reinigung, München: Oldenbourg 1967; Linfield, Anionic Surfactants, New York: Dekker 1974, 1976; Longman, The Analysis of Detergents and Detergent Products, London: Wiley 1975; Milwidsky, Practical Detergent Analyses, New York: MacNair-Dorland 1970; Mukerjee u. Mysels, Critical Micelle Concentrations of Aqueous Surfactant Systems (NSRDS-NBS 36), Washington: US Dept. Commerce 1971; von Nagel, Indanthren, Komplexfarbstoffe, Tenside (Schriftenreihe des Firmenarchivs der BASF 2), Ludwigshafen: BASF 1968; Pollution by Detergents. The Determination of the Biodegradability of Anionic Synthetic Surface Active Agents, Paris: OECD 1972; Rosen u. Goldsmith, Systematic Analysis of Surface-Active Agents, New York: Wiley 1972; Schick, Non-ionic Surfactants, New York: Dekker 1967; Schönborn, Untersuchungen zur analytischen Bestimmung u. zum biologischen Abbau nichtionischer Tenside im Abwasser, Berlin: E. Schmidt 1966; Schönfeldt, Grenzflächenaktive Äthylenoxid-Addukte, Darmstadt: Steinkopff 1976; Shinoda, Solvent Properties of Surfactant Solutions, New York: Dekker 1967; Shinoda et al., Colloidal Surfactants, New York: Academic Press 1963; Sisley, Encyclopedia of Surface-Active Agents (2 Bde.), New York: Chem. Publ. Co. 1952, 1964; Snell-Ettre 11: 322–406; Sittig, Detergent Manufacture 1976, Park Ridge: Noyes 1976; Swisher, Surfactant Biodegradation, New York: Dekker 1970; Ullmann 16: 724–742; Waschmittelchemie, Heidel-

berg: Hühlig 1976; s. a. \*Detergentien, \*Seifen, \*Waschmittel, \*Abwasser.

**Ztschr. u. Serien:** Advances in Colloid and Interface Science, Amsterdam: Elsevier (seit 1967); Tenside Detergents, München: Hanser (seit 1964); Tensid-Kalender (früher: Seifen-Industrie-Kalender, Hrg.: Heller), München: Hanser. — **Organisationen:** Deutscher Ausschuss für grenzflächenaktive Stoffe (DAGSt) im \*Verband der Chemischen Industrie, 6000 Frankfurt; Comité International des Dérivés Tensio-Actifs (CID), 5, Bd. de Latour-Maubourg, F-75007 Paris (17 Mitgliedsländer, vgl. Dürig, Chem. Rdsch. 25 (1972) 1069 u. Großmann, SÖFW 101 (1975) 521 ff., 579 f.).

**B.:** AKZO; Atlas Chemie; Bärlocher; BASF; Baumeier; Bayer; Blau; Borregaard; Brenntag; Compagnie Française de Produits Industriels; Condea; Croda; Drew; Du Pont; Erbslöh; Goldschmidt; Grünau; Hefti; Henkel; Hoechst; Hüls; ICI; Italcold; Jefferson; Krahn; Monsanto; Produits Chimiques de la Montagne Noire; Rewo; Rhône-Poulenc; Rudolf & Co. KG, 8192 Geretsried; Shell; Zschimmer & Schwarz.

**Tensilan** ®. Drag. mit Perazindimalonat u. Propanthelinbromid gegen Magen-Darm-Spasmen.  
**B.:** Desitin.

**Tensionorm** ®. Tabl. mit Theobromin, Papaverin, Atropinsulfat, Phenobarbital-Natrium u. Aminophenazon gegen Hypertonie.

**B.:** Lorenz KG, Fabrik Pharmazeutischer Präparate, 4300 Essen.

**Tensocalm** ®. Tabl. mit 6-Chloro-2-cyclohexyl-3-oxo-5-isindolinsulfonamid (Clorexolon), Levomepromazinmaleat u. Kaliumchlorid gegen Hypertonie.

**B.:** Rhodia Pharma.

**Tentronit** ®. Phenoplast-Lackrohstoff der BASF.

**Tenuate** ®. Depot-Tabl. mit 2-(Diäthylamino)-propiofenon-hydrochlorid (Amfepramon) gegen Übergewicht u. Fettsucht.

**B.:** Merrell.

**Teoclat**. Freie internat. Kurzbez. für 8-Chlortheophyllinat als Salzkompone. — *E* teoclato

**Tepa** ®. Fixiersalz für techn. Fotopapiere.

**B.:** Agfa-Gevaert.

**TEPA**. Engl. Abk. 1. für \*Tetraäthylenpentamin, 2. für Triäthylenphosphoramid (Tris(1-aziridinyl)-phosphinoxid),  $(C_2H_4N)_3P \rightarrow O$ , eine als Cytostatikum vorgeschlagene alkylierende Substanz, s. Ehrhart-Ruschig S. 1774, 1776, 1797.

**Tephrit**. Ein zu den Feldspat-Basalten gerechnetes Erstarrungsgestein, *D.* 2,6–3,0, das zur Herst. von Pflastersteinen u. Schotter verwendet wird. — *E* tephrite

**Tephroit**,  $Mn_2SiO_4$ . Rotes bis graues, rhomb. Manganmineral, kontaktmetasomat.-regionalmetamorph; *D.* 4,1, Härte 5,5–6; kommt z. B. in New Jersey vor. Name von griech.: tephra = Asche (1850). — *E* tephroite

**Lit.:** Ramdohr-Strunz, S. 634.

**Tephrosin**,  $C_{23}H_{22}O_7$ , *MG.* 410,41, Formel s. bei \*Rotenoide. Krist., *F.* 197–198°, unlösl. in Wasser, wenig lösl. in Methanol, gut lösl. in

Chloroform, Äther u. Aceton. Das in \*Derris-Tephrosia- u. Lonchocarpus-Wurzeln vorkommende T. wird wie \*Rotenon gegen beißende Insekten eingesetzt, ist aber schwächer insektizid als dieses. — *E* tephrosin  
**Lit.:** s. \*Rotenoide.

**Tepidone** ®. Vulkanisationsbeschleuniger auf der Basis von Natriumdibutyldithiocarbamat gelbliche wss. Lösung.

**B.:** Du Pont.

**Tepilta** ®. Suspension bzw. Tabl. mit Oxetacarin Aluminiumhydroxidgel u. Magnesiumhydroxid bzw. -carbonat gegen akute u. chron. Gastritiden.  
**B.:** Wyeth.

**Teplamid**. Polyamidgranulat, das in der DDR durch Rückgewinnung aus Polyamid-Verschleißabfällen hergestellt wird.

**B.:** VEB Textil- u. Plastverpackung, DDR-8000 Dresden.

**TEPP**. Engl. Abk. für Tetraäthylpyrophosphat (Tetraäthylidiphosphat),  $(H_3C_2O)_2P(O)-O-P(O)(OC_2H_5)_2$ , *MG.* 290,20. Farblose, hygroskop. Fl., *D.* 1,185, *Kp.* 124° (1 Torr), bei 170 bis 213° Zers. unter Bldg. von Äthylen. Das allg. mit Hexaäthyltetraphosphat etc. verunreinigte Prod. ist mischbar mit den meisten org. Lsgn. u. mit Wasser, in dem es allerdings hydrolysiert wird. TEPP wurde als Insektizid u. Aphizid gegen Blattläuse u. Spinnmilben eingesetzt, medizin. auch als Mydriatikum; es ist für den Menschen sehr giftig (MAK-Wert 0,05 mg/m³); da es durch die Haut eindringen kann, müssen beim Versprühen od. Verspritzen Schutzmasken bzw. Schutzkleider getragen werden. TEPP wurde 1854 von Moschnin erstmals synthetisiert, doch erst 1939 entdeckte \*Schrader die insektiziden Eig., vgl. a. \*Hexaäthyltetraphosphat.

**Lit.:** Kirk-Othmer 11: 699–700; Perkow, Die Insektizide, Heidelberg: Hühlig 1968, S. 297–299; Schrader, Die Entwicklung neuer insektizider Phosphorsäure-Ester, Weinheim: Verl. Chemie 1963, S. 64 bis 79; Winnacker-Küchler (3.) 4: 714, 716; s. \*Phosphorsäureester.

**Teppiche** (von persisch: taftan = Weben, \*Tapeten). Bez. für zu \*Textilien zählende Fußbodenbeläge od. Wandbehänge, die aus Wolle, Haargarn, Chemiefasern, seltener auch aus Seide durch manuelles od. maschinelles Knüpfen od. Weben hergestellt werden — der bisher älteste T. stammte aus dem 5.–3. Jh. vor Christus. Man unterscheidet bei den T. sog. glatte T., mit fester, grober Kette u. grobem (meist farbigem) Schuß gewebt, u. sog. Flor-Teppiche. Diese können geknüpft (Knüpf-T., mit bis zu 450 000 Knoten/m², bei Seiden-T. bis 1 Mio. Knoten pro m²), gewebt (Web-Flor-T. mit geschlossenen Schlingen, z. B. Bouclé-T., od. aufgeschnittenen Flornoppen, z. B. Velours-T.) od. genadelt sein. Letztere, die sich steigender Beliebtheit erfreuen (1972 bereits 60% aller textilen Bodenbeläge

# Surfactant

From Wikipedia, the free encyclopedia  
(Redirected from Tenside)

*This article is about surfactants in general. For the compound produced by alveolar cells, see pulmonary surfactant.*

**Surfactants**, also known as **tensides**, are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids.

## Contents

- 1 Etymology
- 2 Operation and effects
- 3 Applications and sources
- 4 Classification
- 5 External links
- 6 See also

## Etymology

The term *surfactant* is a blend of "**surface acting agent**". Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water. The term surfactant was coined by Antara Products in 1950.

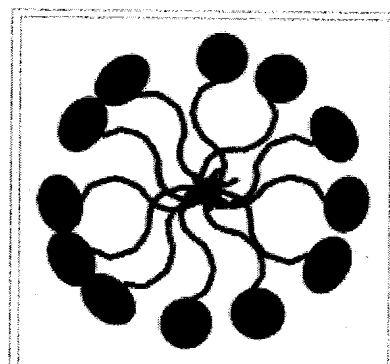
In Index Medicus and the United States National Library of Medicine, "surfactant" is reserved for the meaning *pulmonary* surfactant (see "alveoli" link below). For the more general meaning, "surface active agent" is the heading.

The most common, biological example of surfactant is that coating the surfaces of the Alveoli, the small air sacs of the lungs that serve as the site of gas exchange.

## Operation and effects

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

Thermodynamics of the surfactant systems are of great importance, theoretically and practically. This is because surfactant systems represent systems between ordered and disordered states of matter. Surfactant solutions may contain an ordered phase (micelles) and a disordered phase (free surfactant molecules and/or ions in the solution).



A micelle - the lipophilic ends of the surfactant molecules dissolve in the oil, while the hydrophilic charged ends remain outside, shielding the rest of the hydrophobic micelle

Ordinary washing up (dishwashing) detergent, for example, will promote water penetration in soil, but the effect would only last a few days (although many standard laundry detergent powders contain levels of chemicals such as sodium and boron, which can be damaging to plants, so these should not be applied to soils). Commercial soil wetting agents will continue to work for a considerable period, but they will eventually be degraded by soil micro-organisms. Some can, however, interfere with the life-cycles of some aquatic organisms, so care should be taken to prevent run-off of these products into streams, and excess product should not be washed down gutters.

## Applications and sources

Surfactants play an important role in many practical applications and products, including:

- Detergents
- Fabric softener
- Emulsifiers
- Paints
- Adhesives
- Inks
- Anti-fogging
- Soil remediation
- Wetting
- Ski wax
- Snowboard wax
- Foaming
- Defoaming
- Laxatives
- Agrochemical formulations
  - Herbicides
  - Insecticides
- Quantum dot coating
- Biocides (sanitizers)
- Hair conditioners (after shampoo)
- Spermicide (nonoxynol-9)
- Used as an additive in 2.5 gallon fire extinguishers

Surfactants are also naturally secreted by type II cells of the lung alveoli in mammals.

## Classification

A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

Some commonly encountered surfactants of each type include:

- Ionic
  - Anionic (based on sulfate, sulfonate or carboxylate anions)
    - Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and other alkyl sulfate salts
    - Sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES)
    - Alkyl benzene sulfonate
    - Soaps, or fatty acid salts
  - Cationic (based on quaternary ammonium cations)
    - Cetyl trimethylammonium bromide (CTAB) a.k.a. hexadecyl trimethyl ammonium bromide, and other alkyltrimethylammonium salts
    - Cetylpyridinium chloride (CPC)
    - Polyethoxylated tallow amine (POEA)
    - Benzalkonium chloride (BAC)

- Benzethonium chloride (BZT)
- Zwitterionic (amphoteric)
  - Dodecyl betaine
  - Dodecyl dimethylamine oxide
  - Cocamidopropyl betaine
  - Coco ampho glycinate
- Nonionic
  - Alkyl poly(ethylene oxide)
  - Copolymers of poly(ethylene oxide) and poly(propylene oxide) (commercially called Poloxamers or Poloxamines)
  - Alkyl polyglucosides, including:
    - Octyl glucoside
    - Decyl maltoside
  - Fatty alcohols
    - Cetyl alcohol
    - Oleyl alcohol
  - Cocamide MEA, cocamide DEA, cocamide TEA

## External links

- **(English)** Surfactants explained for Parents
- Sigma-Aldrich: Surfactants - structures, information, and application

## See also

- Anti-fog

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Categories: Colloidal chemistry | Cleaning product components | Surfactants

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# **ANNEX III**

# **SYNTHETIC POLYMERIC MEMBRANES**

**A Structural Perspective**

**Second Edition**

**ROBERT E. KESTING  
IRVINE, CALIFORNIA**

**A Wiley-Interscience Publication**

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*This book is dedicated to Loeb and Sourirajan on the occasion of the twenty-fifth anniversary of their invention of the first integrally skinned, hyperfiltration membrane—an event which not only focused scientific attention upon the advantages of membranes with inhomogeneity in depth but also served as the instrument that heralded the advent of the golden age of membranology.*

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# 7 PHASE-INVERSION MEMBRANES

*Phase inversion* refers to the process by which a polymer solution (in which the solvent system is the continuous phase) *inverts* into a swollen three-dimensional macromolecular network or gel (where the polymer is the continuous phase). In thin-film form designed for use as a barrier layer, such a gel constitutes a *phase-inversion membrane*.

## 7.1 MECHANISM OF PHASE INVERSION

Phase inversion either begins with a molecularly homogeneous single-phase solution (Sol 1) which at some point prior to gelation undergoes a transition into a heterogeneous solution of molecular aggregates consisting of two interdispersed liquid phase (Sol 2), or it begins directly with Sol 2.

In other words, there are two possible reaction sequences for phase inversion:

- (1) Sol 1  $\rightarrow$  Sol 2  $\rightarrow$  Gel or
- (2) Sol 2  $\rightarrow$  Gel

The essence of phase inversion is the appearance in a polymer solution of two interdispersed liquid phases followed by gelation (Fig. 7.1).

The micellar structure which exists in the primary gel, that is, the gel which exists immediately following the Sol 2  $\rightarrow$  gel transition, differs only infinitesimally from that of Sol 2 just prior to gelation. Therefore, since the structures of Sol 2 and of the primary gel are virtually identical, Sol 2 is conceded structural as well as temporal primacy over the gel.<sup>2</sup> In other words, the structure and function of the final phase-inversion membrane is primarily controlled by adjustments to the Sol 2 structure and only secondarily by modification of the primary gel once the latter has formed.

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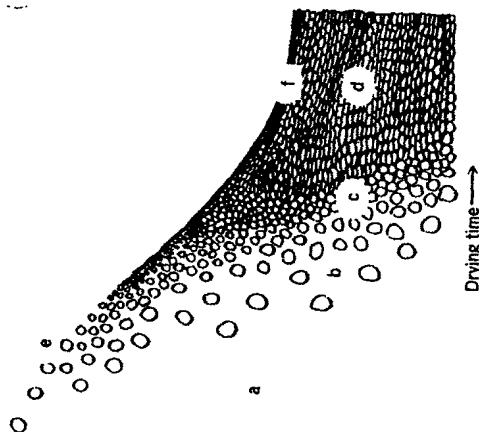


FIGURE 71. Mechanism of formation of phase-inversion membranes: (a) Sol 1; (b) Sol 2; (c) primary gel; (d) secondary gel; (e) air-solution interface; (f) skin (adapted from Kesting<sup>1</sup>).

The dispersed phase of Sol 2 consists of spherical droplets or micelles which are coated with polymer molecules. The composition in the interior of the micelles and in the continuous phase will differ from case to case and depends upon the nature of whatever variation of the phase-inversion process is being employed. The reader may find it helpful at this junction to consider the phenomenological model originally developed by Cahn<sup>3</sup> to describe the two-phase structures of metal alloys and more recently also used in conjunction with polymer blends. This model explains the appearance of isotropic interdispersed domains in terms of the decomposition of the *spinodal*, that is, the metastable region of the polymer volume fraction versus temperature curve and yields some insight into the reasons why *uphill* diffusion, that is, diffusion against the concentration gradient, occurs in phase-inversion solutions. Sol 2 is present when some factor either promotes separation into two phases from one phase and/or prevents two phases from recombining into a single phase. It is expedient to entitle this factor *incompatibility*, and to discuss the subdivisions of the phase-inversion process in terms of the various reasons for incompatibility. In the sections to follow, four phase-inversion processes are discussed: the *dry* process, the *wet* process, the *thermal* process, and the *polymer-assisted* process.

## 7.2 THE DRY PROCESS

The *dry* or *complete evaporation* process is the oldest and easiest to interpret of the phase-inversion processes. It can be followed by reference to a typical cellulose nitrate (CN) casting solution (Fig. 7.2a). Final membrane thickness is only a frac-

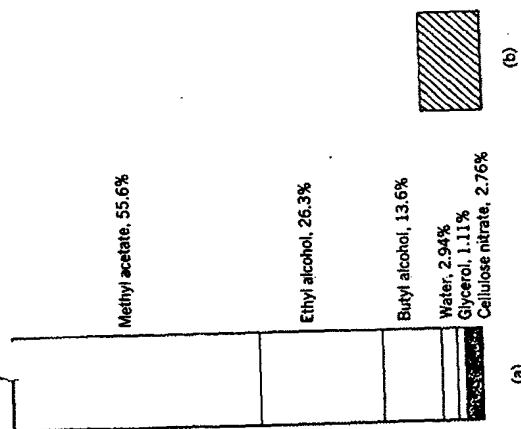


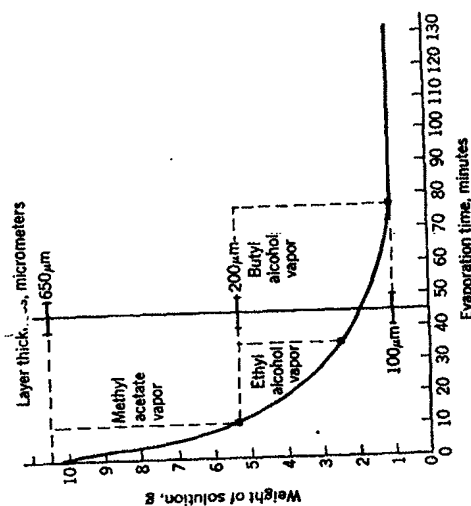
FIGURE 72. (a) Solution components and (b) resultant membrane with 85% void volume depicted as layers whose thickness corresponds to their concentrations (from Maier and Scheuermann<sup>4</sup>).

tion of the as-cast thickness owing to solvent loss and the resultant increase in the concentration of polymer per unit volume. However, because of the inclusion of voids, it is substantially greater than the thickness of a dense membrane containing an equivalent amount of polymer (Fig. 7.2b). The weight and loss of depth as a function of evaporation time of another solution are shown in Table 7.1 and Figure 7.3. This system can be used to exemplify the various macroscopically observable stages involved in the formation of membranes by the dry process.

1. Loss of volatile solvents and the inversion of a clear one-phase solution into a turbid two-phase (Sol 2) solution. Alternatively, the solution may be a turbid Sol 2 type to begin with. Ease of processing and reproducibility are enhanced if the solution begins with a Sol 1 or at least a Sol 2 which is somewhat removed from the point of incipient gelation. Thus in most cases it is desirable to formulate a Sol 1 which does not invert into a Sol 2 until some time after it has been cast.
2. Gelation. This is accompanied by a diminution in the reflectivity of the cast solution.
3. Contraction of the gel with or without syneresis. In the case of skinless membranes, syneresis causes expressed liquid to appear at the air-solution interface which can be at both surfaces if the membrane is cast on a porous support. In the case of membranes which are skinned at the air/solution interface, syneresis occurs downward into the porous support or, where no such support exists, it does not occur at all. In such a case drying can be a slow process since it will require the diffusion of vapor rather than liquid through what may be a relatively impenetrable skin layer.

TABLE 71 DECREASE IN CASTING-SOLUTION WEIGHT AND THICKNESS WITH DRYING TIME<sup>a,b</sup>

Evaporation Time (min)	Solution Weight (g)	Thickness of Nascent Membrane ( $\mu\text{m}$ )
0	10.5	650
0.40	9.5	—
0.83	9.0	500
1.58	8.5	—
2.08	8.0	450
2.8	7.5	350 <sup>c</sup>
4.0	7.0	300
5.16	6.5	280
6.67	6.0	250
8.25	5.5	220
10.50	5.0	200
13.16	4.0	170
20.33	3.5	155
24.16	3.0	150
31.0	2.5	135
35.5	2.0	—
43.0	1.75	125
47	1.50	—
54	1.25	115
74	1.25	115
130	0.99	—
900	0.82	100

<sup>a</sup>From Maier and Scheuermann.<sup>4</sup><sup>b</sup>Evaporation at  $21 \pm 1^\circ\text{C}$  in a  $62 \pm 2\%$  relative humidity environment. Original casting solution: 5% cellulose nitrate, 54.2% methyl acetate, 23.7% ethyl alcohol, 12.3% butyl alcohol, 3.3% water, and 1.5% glycerol.<sup>c</sup>From this point on values refer to the thickness of the gel exclusive of the layer of expelled liquid.FIGURE 73. Decrease in casting solution weight and thickness with evaporation time (from Maier and Scheuermann<sup>4</sup>).

membrane should be handled unless it is completely dry because it is subject to shrinkage and warpage while in a plasticized condition.

The sequence of events on the colloidal level which corresponds to the five macroscopically observable stages has been deduced both from the nature of the gel network in the finished membrane<sup>1-5</sup> and from the ghosts of the nascent membrane, that is, the frozen and lyophilized nonvolatile remnants of the membrane in its various formative phases<sup>6</sup> (Fig. 7.4). The polyhedral cell structure of the final membrane gel is considered to be an immobilized and flattened version of the sol precursors which exist in the solution immediately prior to the sol  $\rightarrow$  gel transition. As the loss of volatile solvent progresses, the solvent power of the solution, that is, its capacity for retaining the polymer in a Sol 1 decreases. If only polymer and solvent are present then at least three situations are possible.

1. Separation into two liquid phases may not occur prior to gelation. This would be the case if polymer and solvent are infinitely miscible. Even after gelation the solvent will continue to act as a plasticizer, which when combined with the effect of gravity can lead to a collapse and densification of the gel, resulting ultimately in a dense film.
2. Phase separation may occur prior to gelation if there is only limited solubility of the polymer in the solvent. However, even in this case residual solvent can act as a plasticizer and dense or nearly dense (low porosity) films may result.
3. In those cases in which P-P interaction is unusually strong, such as, for example, in the evaporation of solutions of nylon 6,6 in 90% formic acid,<sup>7</sup> gelation will occur with the formation of strong virtual (perhaps crystalline) cross-links. Such a gel can overcome the combined effects of plasticization and gravity so that

4. Capillary depletion. Here the largely nonsolvent liquid encompassed by the gel departs leaving behind empty capillaries. As this happens the membrane opacifies, usually with the formation of beautiful snowflake patterns that gradually fill in until the entire membrane becomes opaque. The reason for opacification is light scattering by the micrometer-sized empty voids. On the other hand, those membranes which contain voids that are less than  $0.5 \mu\text{m}$  in diameter can be opalescent or clear. Subtle differences in void size can sometimes also be discerned from the turbidities of the dry gels once they have been wet by water.

5. Loss of residual nonsolvent (final drying). Depending on such factors as the volatility and concentration of the residual liquids left in the membrane after take-up, the amount of membrane on the roll, and storage temperature, final drying can vary between 2 weeks and 6 months. It is also possible to take up the membrane in an essentially dry condition by passing it over heated rollers. In either case, no



FIGURE 7.4. SEM photomicrograph of lyophilized micelles in the nascent skin of a dry cellulose acetate hyperfiltration membrane (from Kesting<sup>5</sup>); © 1973).

its porosity is maintained throughout complete evaporation. In the lattermost case, after phase inversion has occurred and prior to gelation, the sol structures exhibit long-range order. Virtually any disruption of this order or *nucleation* in the sol by, for example, rapid agitation or even fine filtration will result in a final membrane with larger pores sizes than would have otherwise resulted from gelation of the undisturbed sol.

Both the interior of the micelle and the continuous phase of a two-component system consist of polymer-poor regions whereas the micellar wall consists of polymer-rich regions (Fig. 7.5). In the latter, P-P interaction predominates over P-S interactions. Most dry-process casting solutions, however, consist of three or more components: polymer, volatile solvent, and pore former(s) from the nonsolvent side of the polymer-solvent interaction spectrum (Chapter 5). The nonsolvent should be substantially less volatile than the solvent—a practical rule of thumb is a 30–40°C minimum difference in boiling points between the two. Although Sol 1 is homogeneous on the colloidal level (Fig. 7.6a), compatibility decreases as evaporation proceeds. Eventually, the solvent power of the remaining solvent system is insufficient to maintain Sol 1, and inversion into Sol 2 occurs (Fig. 7.6b). Most of the polymer molecules distribute themselves about the micelles which have been formed, so that relatively few (perhaps 0.5%) are left dispersed in the liquid matrix containing the micelles. The interior of the micelle in this case consists of a liquid with a high concentration of the nonsolvent components of the casting solution. In the typical dry process the fundamental reason for incompatibility which leads to

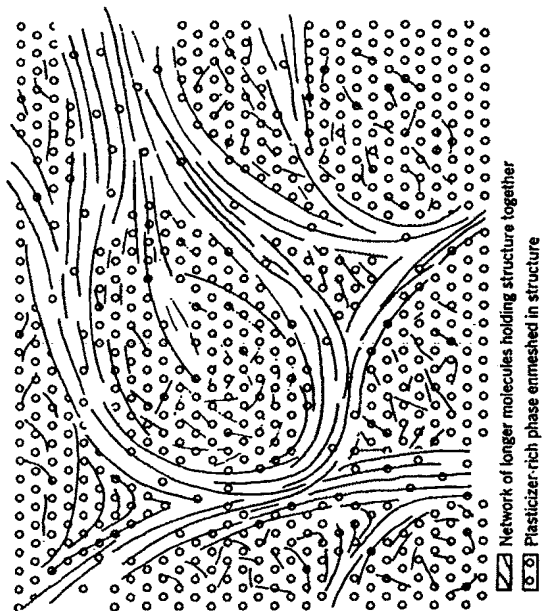


FIGURE 7.5. Theoretical structure of a plastic containing a nonsolvent plasticizer (from Spurlin, et al.<sup>6</sup>); © 1946).

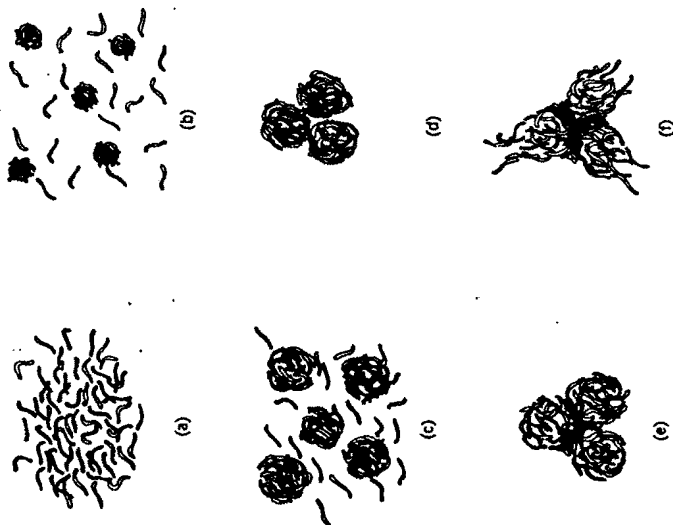


FIGURE 7.6. Membrane formation process (adapted from Maier and Scheuermann<sup>7</sup>).

phase inversion, gelation, and the maintenance of gel porosity in the casting solution which act to collapse the gel, is the presence of nonsolvent in the casting solution and/or strong P-P interaction forces. In other words, in the dry process incompatibility is an *internal* characteristic of the system. Inasmuch as solvent loss continues after phase inversion, the spherical micelles approach one another (Fig. 7.6c), eventually making contact in the initial phase of gelation (Fig. 7.6d). As the gel network contracts, the micelles deform into polyhedra and the polymer molecules diffuse into the walls of neighboring micelles causing an intermingling of polymer molecules at the interface (Fig. 7.6e). Finally, if the walls are sufficiently thin, for example, when a high initial concentration of components other than polymer and solvent causes the formation of numerous micelles with a large total surface area, contraction causes a tearing of the walls which then retract and form the hose-like skeleton which constitutes the gel network (Fig. 7.6f). A similar phenomenon occurs during the bursting of soap bubbles<sup>9</sup> and the formation of open-celled polyurethane foams. It can happen, however, that micelles are covered with such a thick coating of polymer that rupturing of cell walls is somewhat hindered or entirely inhibited. In such a case either mixed open-cell and closed-cell or closed-cell structures result. The principal factors which determine the porosity and pore-size characteristics of dry-process membranes are:

1. Polymer volume concentration in Sol 2 which is inversely proportional to gel porosity.
2. Ratio of nonsolvent volume/polymer volume in Sol 2 which is directly proportional to gel porosity.
3. Difference in boiling points between solvent(s) and nonsolvent(s) which is proportional to porosity and pore size.
4. Relative humidity which is proportional to porosity and pore size.
5. The presence of more than one polymer with less than perfect compatibility increases porosity.
6. The presence of a high-MW polymer tends to increase porosity because high-MW polymers tend to be less compatible and thus gel at an earlier stage.

Because dry-process solutions employ nonsolvent pore formers, the capacity of the solvent system to tolerate high concentrations of polymer is severely limited. In spite of this the casting solution must be sufficiently viscous to permit its handling during flat-sheet and tubular casting or hollow-fiber spinning operations. This dilemma is resolved by utilizing high-MW polymers which although slightly less soluble than their low-MW counterparts do contribute significantly more to solution viscosity. However, most engineering plastics are available only in the low- to intermediate-MW ranges because they are designed for melt processing applications such as injection molding. This can and often does limit the application of the dry process. Methods for circumventing this obstacle include the preparation of special grades of high-MW polymers,<sup>10</sup> the utilization of viscosity enhancers

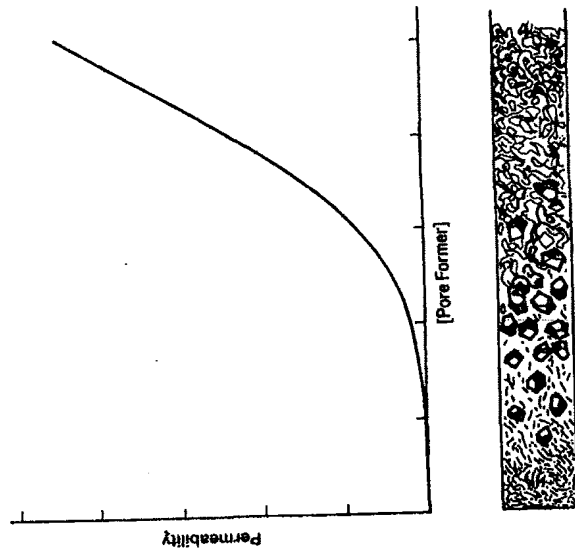


FIGURE 7.7. Relationship between cell type, skin thickness, concentration of pore former, and permeability in phase-inversion membranes.

such as a second polymer<sup>11,12</sup> or finely divided colloidal silica, and casting at low temperatures.

A summary of the effects upon cell structure and porosity, and hence on the permeability of dry-process membranes which can result from variations in polymer and/or nonsolvent concentrations in the casting solution, is schematically depicted in Figure 7.7. In the absence of any nonsolvent pore former or strong P-P interaction, phase inversion does not take place (Sol 1  $\rightarrow$  gel) so that a dense high-resistance membrane or film is formed. Such a structure as a first approximation consists of a single dense skin layer. With low concentrations of nonsolvent, membranes possessing closed cells, low porosity, and substantial resistance to material transport are encountered (Fig. 7.8). However, the thickness of the dense skin layer is substantially diminished. At intermediate concentrations of nonsolvent a mixture of open and closed cells is formed (Fig. 7.9). The dense skin layer has thinned considerably and a thin transition layer is discernible which consists of closed cells which are intermediate in polymer density between those of the dense skin layer and those of the porous open-celled substructure which is found in the bulk of the membrane. Permeability is low but measurable at this point. At high concentrations of nonsolvent a bilayered structure is found which is comprised of a thin skin and a porous substructure that consists entirely of open cells (Fig. 7.10). There is a break in the curve of permeability versus porosity at that concentration at which mixed open and closed cells give way to open cells. As the concentration of non-

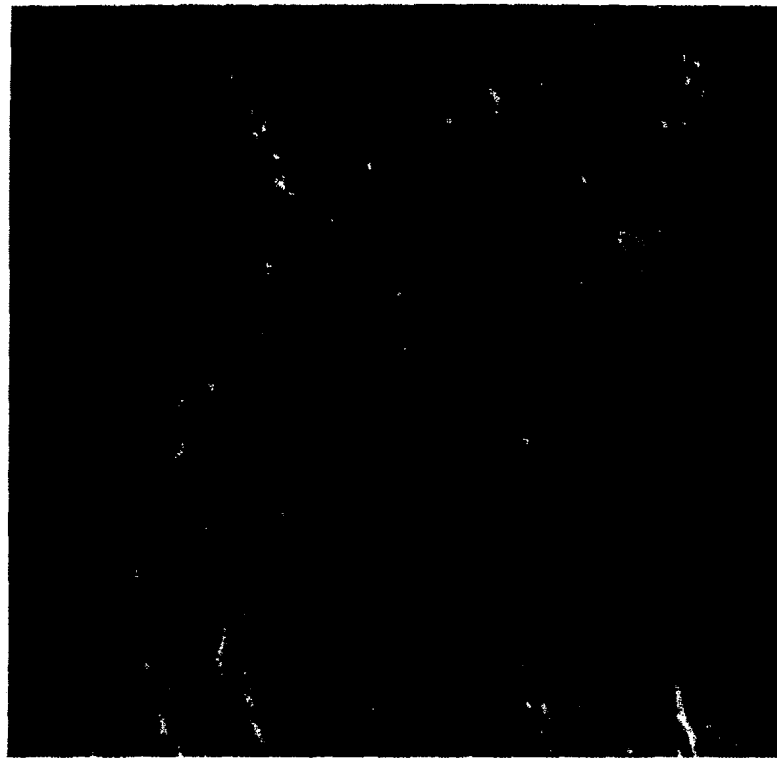


FIGURE 7.8. SEM photomicrograph of a cross section of a dry cellulose acetate membrane with closed cells.

solvent is increased beyond this point, skin thickness decreases and permeability increases. Eventually, however, the skin becomes sufficiently thin that its integrity is breached in places and the porous substructure becomes visible (Fig. 7.11). Ultimately, at very high concentrations of nonsolvent, the dense skin layer is absent altogether and both surface and interior regions consist only of open cells with tears in the walls, that is, the porous surfaces of microfiltration membranes are encountered. As nonsolvent concentration is increased even beyond this point, cell and pore size increase further as does permeability. Eventually, even the integrity of the porous substructure cannot be maintained (Fig. 7.12). If structures with pore sizes greater than about  $5\text{ }\mu\text{m}$  are desired, processes other than phase inversion are employed.

The interrelationship between  $\Delta\text{ bp}$  (bp nonsolvent - bp solvent) of the two solvents acetone (bp  $56^\circ\text{C}$ ) and dioxolane (bp  $75^\circ\text{C}$ ) and the levels of a single nonsolvent isobutanol (bp  $110^\circ\text{C}$ ) required to produce equivalent skinned mem-

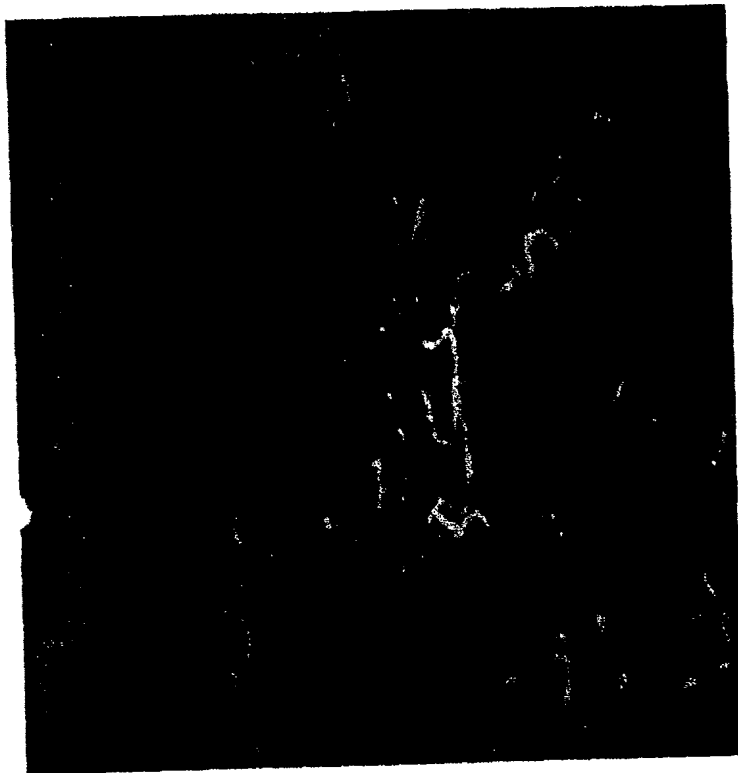


FIGURE 7.9. SEM photomicrograph of a cross section of a dry cellulose acetate membrane with a transition layer.

branes (as deduced from their equivalency in permeability and permselectivity) is shown in Table 7.2

Both solvent and nonsolvent evaporate simultaneously. Therefore, if a critical solvent-nonsolvent ratio must be reached before gelation occurs, a less volatile solvent requires a higher initial concentration of a given nonsolvent to reach this ratio at a given porosity than will a more volatile solvent. In like manner, the concentration of nonsolvent in the casting solution required to achieve a given porosity is inversely related to its volatility.

Bjerrum and Manegold<sup>13</sup> were among the first to observe the influence of the composition of the atmosphere above the desolvating solution upon membrane structure and function. The presence of a high concentration of solvent vapor retards gelation, whereas high temperatures and air velocities will hasten it. *Skinning* is enhanced by high air-flow rates and high polymer concentrations. The effect of atmospheric moisture is to hasten gelation which in turn acts to increase average pore size and permeability (Table 7.3). The inclusion of water in the casting solution has a very pronounced effect in those cases in which water plays a nonsolvent role

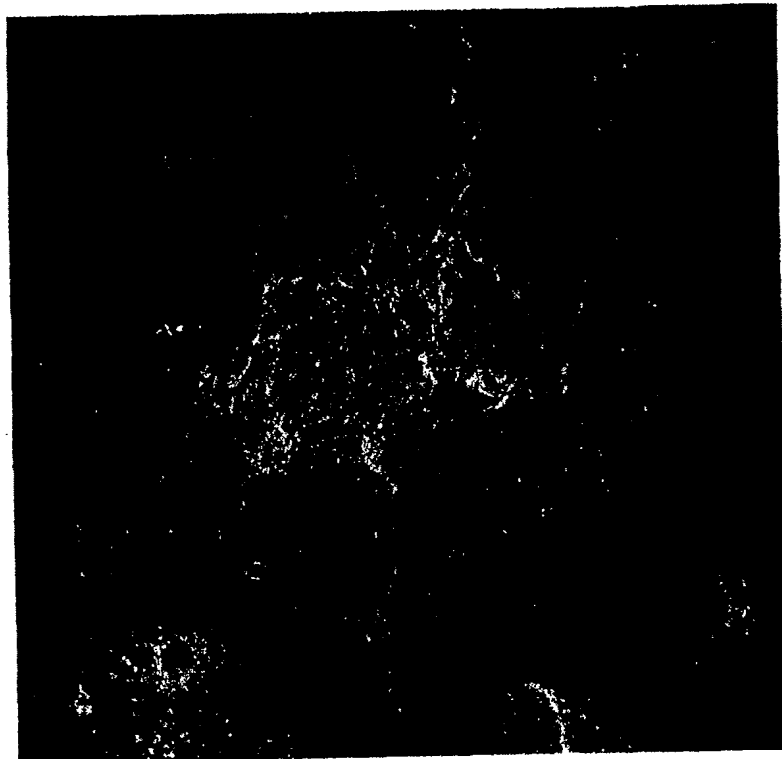
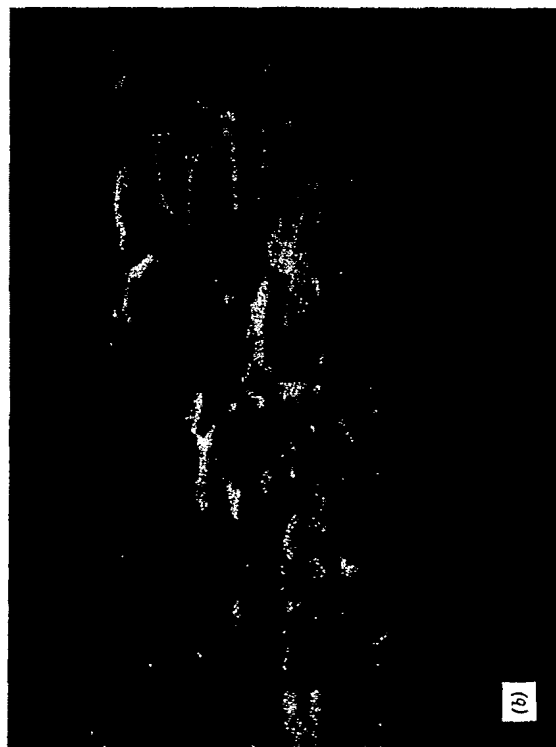


FIGURE 7.11. SEM photomicrograph of the top surface of a dry cellulose acetate membrane with a nonintegral skin.

(Table 7.4). In hydrophobic sols water acts both to hasten gelation and to increase the size of voids in the gel structure. This is attributable to two factors: (1) a high degree of incompatibility with the solvated polymer component of the casting solution; and (2) high surface tension. Both factors act to cause water to separate from the remainder of the solution and nucleate comparatively large micelles which then result in coarse microgels. The presence of a microgel structure in membranes from polymers such as the cellulose and the polyamides which possess some affinity for water confers the important property of wet-dry reversibility on these membranes.<sup>6</sup> This is so because the magnitude of the capillary forces which come into play upon drying depends on the internal surface area of the membrane which in turn depends on the cell size. Microgel membranes possess large (1–10  $\mu\text{m}$  diameter) cells which means that such membranes have a relatively small internal surface area and as a result will not lose porosity during drying. Ultragel membranes, on the other hand, have small (0.5–0.5  $\mu\text{m}$  diameter) cells and consequently possess a larger internal surface area. Ultragels are therefore more likely to lose



(a)



(b)

FIGURE 7.10. SEM photomicrograph of a cross section of a dry cellulose acetate membrane with open cells: (a) entire cross section; (b) partial cross section at skin surface.

TABLE 7.3 EFFECT OF RELATIVE HUMIDITY UPON PERMEABILITY AND PORE SIZE<sup>a</sup>

Relative Humidity at 20°C (%)	Filtration Time <sup>b</sup> (sec)	Average Pore Diameter (nm)
80	25-40	~600
60	40-60	~500
40	60-80	~400

<sup>a</sup>From Maier and Scheuermann<sup>1</sup><sup>b</sup>For 500 mL H<sub>2</sub>O/12.5 cm<sup>2</sup> at 70 cm HgTABLE 7.4 INFLUENCE OF CASTING SOLUTION WATER CONCENTRATIONS UPON PORE SIZE AND PERMEABILITY OF COLLOIDION MEMBRANES<sup>a</sup>

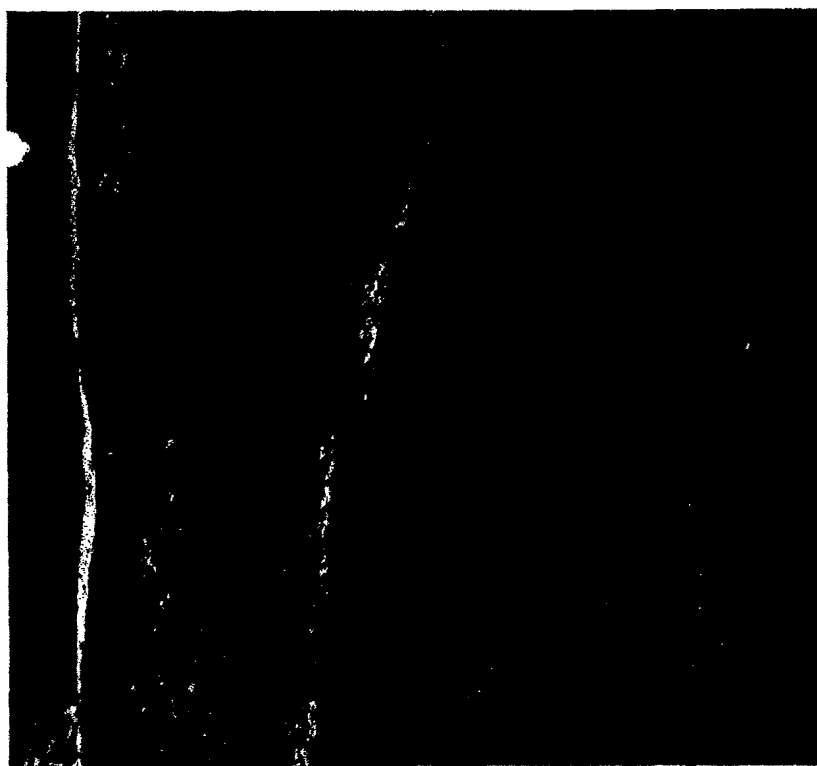
H <sub>2</sub> O Concentration in Casting Solution (%)	Filtration Time <sup>b</sup> (S)	Average Pore Diameter (nm)	Casting-Solution Viscosity at 20°C (cps)
3.3	40	600	2011
0.4	800	30	1813
0.0 (trace)	4000	15	1600

<sup>a</sup>From Maier and Scheuermann<sup>1</sup><sup>b</sup>For 500 mL H<sub>2</sub>O/12.5 cm<sup>2</sup> at 70 cm Hg.

porosity during drying and less likely to be wet → dry reversible. Since the dry process tends to employ more dilute solutions and less compatible pore formers (both of which characteristics promote the formation of microgels) than does the wet process, the former is more likely to produce microgels than the latter. However, there are many exceptions to this rule and it is possible both to produce microgels by a wet process and ultragels by a dry process.

### 7.3 THE WET PROCESS

The wet or combined evaporation-diffusion technique is that variation of the phase-inversion process in which a viscous polymer solution is either (1) allowed to partially evaporate after which it is immersed into a nonsolvent gelation bath where whatever is left of the solvent-pore-former system is exchanged for the nonsolvent or (2) is immersed directly into the nonsolvent gelation bath for the exchange of the solvent system for nonsolvent. The end products of the wet process are water-swollen membranes; moreover, the water content of membranes—the equivalent of porosity in the dry process—is a prime determinant of its functional performance characteristics. *It is therefore fundamental to consider the effects of such variables*

FIGURE 7.12. SEM photomicrograph of a cross section of a dry cellulose acetate membrane with a nonintegral substructure (from Kesting et al.<sup>14</sup>; © 1965).TABLE 7.2 EQUIVALENT NONSOLVENT CONCENTRATIONS IN ACETONE AND DIOXOLANE SOLUTIONS<sup>a</sup> FOR DRY-RO BLEND MEMBRANES OF CA AND THE TMA SALT OF CA 11-BROMOUNDECANOATE

Solvent	Boiling Point (°C)	Δbp (°C)	Nonsolvent Concentration (g IBA/formulation)	Permeability <sup>a</sup> (gal/ft <sup>2</sup> day)	Salt <sup>b</sup> Rejection (%)
Acetone	56	54	38	5.6	97.9
Dioxolane	75	35	54	5.5	97.8

<sup>a</sup>Total polymer concentration, 10% wt/vol; polymer ratio, 6/1 ILF-68CA/TMA salt of CA 11-bromoundecanoate (made from E-383-40 CA with 0.5-DS (quaternary ammonium groups); methanol, 10 g/formulation.

<sup>b</sup>0.5% NaCl feed at 400 psi and 25 ± 1°C.



as casting-solution composition and environmental parameters in terms of their effects upon membrane-water contents.<sup>14,15</sup>

A wet-process solution must be relatively viscous ( $\geq 10^4$  cps) at the moment of immersion in the nonsolvent so that it will retain its integrity throughout gelation. When it is too fluid, the primary gel will be subject to disruption by the weight of the nonsolvent and the uneven forces brought about by the various currents which come into play during immersion. The requirement for high viscosity and hence high polymer concentration is in most cases inconsistent with the attainment of high porosity via the inclusion of nonsolvent pore formers. Therefore, when they are required, pore formers which are utilized in wet-process casting solutions are frequently chosen from the swelling agent—weak solvent side of the polymer-solvent interaction spectrum (Chapter 5). Moreover, the presence of pore formers within the casting solution prior to its immersion into a nonsolvent gelation bath is not a requirement of every wet-process solution. In many instances, particularly when nonvolatile solvents with a strong affinity for the nonsolvent in the gelation bath are utilized, the phase-inversion sequence Sol 1  $\rightarrow$  Sol 2  $\rightarrow$  gel is evoked by the simple act of immersion into nonsolvent. In such a case the nonsolvent bath represents an external source of incompatibility and a two-component solution (polymer + solvent) becomes in effect a three-component solution (polymer + solvent + nonsolvent pore former) as a result of the diffusion of the nonsolvent into, and the solvent out of, the nascent membrane gel.

The effect of the strong nonsolvent, water, may be influenced by other components of the casting solution. The presence of lyotropic salt swelling agents from the Hofmeister series causes the aggregation of water molecules about the electrophilic cations, thereby considerably modifying the properties of the water so affected.<sup>14</sup> The result of this interaction is to change the role of water from that of a nonsolvent to that of a swelling agent (Table 7.5). Other polar nonsolvents such as the aliphatic alcohols function in much the same manner as water, except that their nonsolvent tendencies are less pronounced. The role of water in the atmosphere and in the solution to effect gross structural irregularities will be discussed later in this chapter.

The effects of increasing the concentration of the weak nonsolvent pore former, ethanol, in a casting solution containing CA and acetone is to increase the porosity of the resultant membranes (Table 7.6, Fig. 7.13). (Because of their excellent solubility, certain cellulosic polymers can be so formulated that their solutions represent exceptions to the rule that wet-process solutions require highly compatible pore formers). As the concentration of ethanol is increased, the values of  $\delta_p$  decrease slightly and the values of  $\delta_h$  increase appreciably, which has the effect of bringing the solution closer to the point of incipient gelation, that is, to the perimeter of the solubility envelope. Since a solution which contains a high concentration of nonsolvent can be presumed to be of the Sol 2 type close to gelation, its immersion into a nonsolvent bath and subsequent gelation will be accompanied by less gel contraction than would occur if the solution were further removed from the perimeter of the solubility map. The result is that porosity and permeability increase as the concentration of pore former increases. Because the pore former is

TABLE 7.5 CASTING SOLUTION WATER-CONCENTRATION EFFECTS\*

Water Concentration <sup>b</sup> (g/for-mulation) <sup>b</sup>	Swelling-Agent Concentration (g ZnCl <sub>2</sub> /for-mulation) <sup>b</sup>	Description of Membrane	Wet Thickness of Unheated Membrane (mm) $\times 10^2$	Gravimetric Swelling Ratio (wet wt/dry wt)	Rate of Water Transport (ml/cm <sup>2</sup> day) <sup>c</sup>	0.6 M NaCl Feed	Salt Retention (%)
0	0	Brittle, opaque (microgel)	5.8	1.47	< 1	—	—
5	0	Brittle, opaque (microgel)	6.4	1.77	< 1	—	—
10	0	Brittle, opaque (microgel)	7.1	1.99	< 1	—	—
15	0	Brittle, opaque (microgel)	8.0	2.35	< 1	—	—
0	5	Clear (microgel)	8.7	2.53	24	16	90.3
5	5	Opalescent (ultragel)	9.0	2.79	34	22.8	97.2
10	5	Opalescent (ultragel)	9.2	2.85	72	48	98.5
15	5	Opalescent, opaque (ultra-gel-microgel)	9.6	2.92	136	82	96.2

\* From Kesting et al.<sup>15</sup>, © 1965.  
<sup>b</sup> Formulation: cellulose acetate, 22.2 g; acetone, 66.7 g (doctor-blade gap, 0.25 mm).  
<sup>c</sup> Rate of water transport and salt retention at 102-atm pressure for heated membranes (86°C for 5 min).

of a nonsolvent type, solution compatibility decreases with increasing ethanol concentration. This leads ultimately to increased diameters in the micelles of Sol 2 and consequently to greater opacity in the final membrane. It is worthy of note that it is only the insufficient  $\Delta$ bp of 23°C between acetone and ethanol which prevents this solution from being a candidate for the dry process. If methyl formate (bp 30°C) or propylene oxide (bp 35°C) had been employed as solvents in conjunction with ethanol as the pore former, this solution could have served in either a wet- or a dry-process mode. If acetone had been utilized as a solvent in conjunction with propanol (bp 97°C) or isobutanol (bp 108°C) as pore formers, the same would of course apply.

The effects of increasing the concentration of the solvent-type pore former, formamide, upon the porosity, optical, and permeability properties of CA membranes are found in Table 7.7. In the first place, the utilization of this solution in the dry-process mode leads to the formation of a dense film. Since both acetone and formamide are solvents, the loss of the more volatile acetone leaves behind a high-boiling solvent, formamide, which plasticizes the CA gel as it evaporates. The fact that  $[\eta]$  increases and both solution and membrane turbidity decrease with increasing concentration of formamide in the acetone-formamide solvent system suggests that solvent power increases as well. Concurrent increases in thickness, porosity, and permeability are attributable to the strong hydrogen-bonding capacity of formamide coupled with its strong affinity for solvating CA. After immersion, desolvation of such solutions is slow rather than rapid because water can associate with formamide by hydrogen bonding, thereby lessening water's role as a strong nonsolvent. The net result appears to be that the Sol 2  $\rightarrow$  gel transition occurs at a reduced rate during which the aggregating mass is more amenable to the infusion of a higher concentration of nonsolvent than would otherwise be possible in the case of a more abrupt Sol 2  $\rightarrow$  gel transition.

The gelation bath temperature also exerts an important influence upon the struc-

TABLE 7.7 PROPERTIES OF SOLS AND GELS FROM ACETONE-FORMAMIDE SOLUTIONS OF CA\*

Formamide Concentration (mol %)	Sol <sup>b</sup> Properties			Gel Properties		
	$[\eta]$ 25°C	Turbidity at 546 $\mu$ m ( $\times 10^{-4}$ )	Turbidity at 546 $\mu$ m ( $\times 10^{-4}$ )	Thickness ( $\mu$ m)	Wet wt	Water Fl (cm/day)
0	0.895	1.6	38.7	36	1.71	No flo
10	0.942	0.9	33.2	43	2.10	No flo
20	0.948	0.6	—	46	3.01	26
30	0.963	0.5	20.7	74	3.44	128
40	—	0.45	7.8	86	3.90	384
50	—	0.45	1.4	94	4.40	1320

\*Adapted from Kesting and Menefee.<sup>17</sup>

<sup>b</sup>15 g E-398-10 CA/100 mL solution.

<sup>c</sup>Distilled-water feed at 40.8 atm and 25°C.

TABLE 7.6 EFFECT OF SWELLING AGENT (ETHANOL) ON THE MEMBRANE-WATER CONTENT\*

Membrane Code No.	Mixed Solvent		Calculated $\delta$ Values of Mixed Solvents		Membrane-Water Content (wt %)
	Ethanol (mol %)	Acetone (mol %)	$\delta_p$	$\delta_h$	
CA-24	20	80	4.99	4.23	50.7
CA-23	30	70	4.93	4.69	50.3
CA-22	40	60	4.86	5.20	53.4
CA-25	46.6	53.4	4.83	5.47	61.2
CA-21	50	50	4.79	5.75	65.8

\*From Chawla and Chang<sup>16</sup>, © 1975.

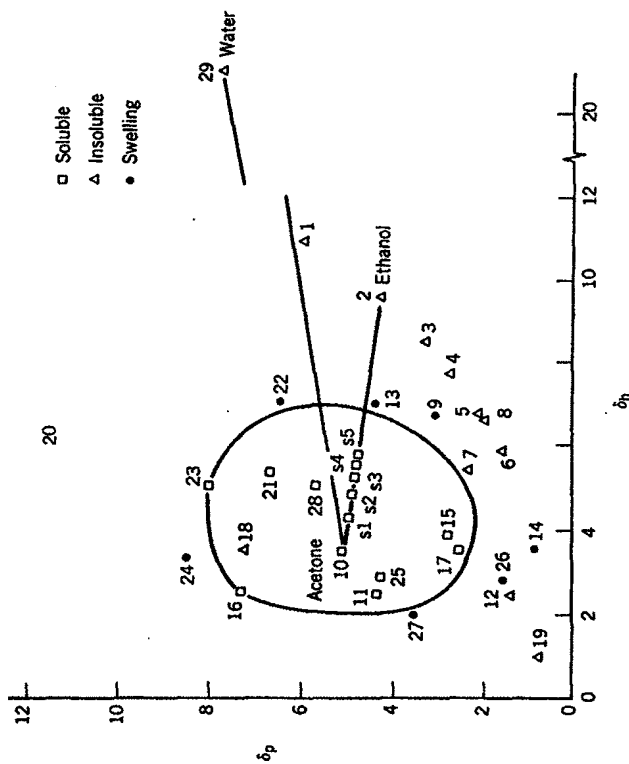


FIGURE 713. Solubility diagram for cellulose acetate. Solvents used: (1) methanol, (2) ethanol, (3) propanol, (4) butanol, (5) 1-pentanol, (6) 1-octanol, (7) 2-octanol, (8) cyclohexanol, (9) benzyl alcohol, (10) acetone, (11) methyl ethyl ketone, (12) diethyl ether, (13) ethylene glycol monoethyl ether, (14) dioxane, (15) tetrahydrofuran, (16) furfural, (17) ethyl acetate, (18) ethyl sulfate, (19) toluene, (20) formamide, (21) *N,N*-dimethyl formamide, (22) diethylene triamine, (23) dimethyl sulfoxide, (24) acrylonitrile, (25) pyridine, (26) chloroform, (27) 1,2-dichloroethane, (28) acetic anhydride, and (29) water (from Chawla and Chang<sup>16</sup>).

ture and function of HF membranes (Table 7.8). Increasing temperature hastens the onset of gelation which in turn results in increased void size, degree of swelling, and permeability, and decreased permselectivity.

Increasing the evaporation (drying) time prior to immersion in the nonsolvent medium causes a decrease in cell size and porosity and hence a decrease in permeability (Table 7.9). Permselectivity first increases and then decreases owing to stress imposed on the skin layer and possibly also to some swelling and rehardening of the skin as the solvent concentration in the nonsolvent bath increases.

The higher the affinity of the gelation medium for the components of the casting solution, the more gradual will be the Sol 2  $\rightarrow$  gel transition and the greater will be porosity in the final membrane. Thus the gelation of a CA solution in methanol will lead to a membrane of higher porosity than the gelation of the same solution in water. Methanol has greater affinity for CA than does water. Conversely, water is a stronger nonsolvent for CA than is methanol. Because the immersion of a casting solution in a strong nonsolvent such as water often leads to a skinned membrane it may be expedient, when a skinless membrane is desired, to immerse the casting solution into a nonsolvent solution which contains some solvent. Likewise, when a skinned membrane is available by any process, the skin may often be removed by immersing it into a nonsolvent/solvent solution. A closely related phenomenon known as *clearing* is utilized to collapse an opaque microporous electrophoresis membrane into a clear dense film so that the electrophoretogram can be read on an optical densitometer without changing the spacial relationships between the various protein fractions. Here the reverse of the dry casting process is employed. Instead of utilizing a volatile solvent and a nonvolatile nonsolvent to gradually decrease compatibility, a volatile nonsolvent and a nonvolatile solvent are employed to gradually increase the affinity of the clearing solution for the membrane substance as drying progresses. Gravity does the rest as the softened but intact gel slowly collapses.

The structure which is at hand immediately following the Sol 2  $\rightarrow$  gel transition in the dry process is known as a primary gel. It is seldom isolated as such because with continued evaporation ( $\pm$  syneresis) and drying the completely consolidated membrane, known as the secondary gel, is ordinarily the only product which is encountered or of interest. This is not usually the case for the wet process, however. Here, after the viscous solution has been gelled by immersion and the solvent system has been removed from the gel, a primary gel membrane which is stable as such for an indefinite period is the result. Such a membrane is easily distinguished from the secondary gels which result after the primary structures have been subjected to various postformation treatments.

As was the case for the dry process, the control of primary gel structure by environmental and especially casting-solution variables permits far greater latitude in the regulation of ultimate structural and performance characteristics of wet phase-inversion membranes than does the modification of primary into secondary gels. Because the properties of the primary gel determine to a large extent those of its secondary counterpart, the former should be considered as the more fundamentally characteristic and important structure in any consideration of the effects of varia-

TABLE 7.8 GELATION-BATH TEMPERATURE EFFECTS<sup>a,b</sup>

Gelation-Bath Temperature (°C)	Membrane Appearance	Viscosity [ $\eta$ ] of Cellulose Acetate in Acetone-Water (66.7:100) <sup>c</sup>	Wet Thickness of Unheated Membrane [(mm) $\times 10^2$ ]	Gravimetric Swelling Ratio of Unheated Membrane (wet wt/dry wt)	Rate of Water Transport mL/cm <sup>2</sup> day <sup>d</sup>	NaCl Feed 0.6 M	Salt Retention (%)
0	Opalescent	0.985	9.2	2.85	84		98.6
10	Opaque	0.940	14.0	3.80	83		97.1
25	Opaque	0.05	22.8	5.80	90		90.1
40	Opaque	0.745	31.0	6.98	118		81.1
					74		
					58		
					50		
					50		

<sup>a</sup>From Kesting et al.<sup>15</sup>; © 1965.

<sup>b</sup>Casting-solution composition: cellulose acetate, 22.2g; acetone, 66.7g; water 10.0g; ZnCl<sub>2</sub>, 5.0g (doctor-blade gap, 0.25 mm). Measured at the corresponding gelation-bath temperature.

<sup>c</sup>Rate of water transport and salt retention at 102 atm pressure for heated membranes (86°C for 5 min).

tions in fabrication parameters, for example, casting-solution composition, upon performance characteristics. Once a primary gel has been formed, it may be utilized as such (particularly for low-pressure applications), or it may be subjected to various physical and/or chemical treatments for conversion into a secondary gel which may be more suitable for a given end use.

Physical modifications of primary gel structures can be effected either to increase or to decrease the porosity (degree of swelling, void volume, water content etc.), pore size, permeability, and permselectivity. The technique utilized to produce porous membranes from dense films can be used to effect an increase in porosity. In this variation of Brown's<sup>18</sup> technique (Chapter 8), an already porous primary gel is immersed in a swelling medium. To set the secondary gel in its more expanded condition the swelling medium is removed, either by exchange with a nonsolvent (nonsolvent-swelling-agent miscibility is essential) or by simple evaporation.

Since this technique adds another step to the fabrication process and is complicated by the leaching of low-molecular-weight polymer from the primary gel by the swelling medium, it is usually circumvented by the reformulation of the casting solution to produce a primary gel with an initially higher void volume. It is frequently encountered, however, as an undesirable factor in the permeation of certain organic solutes which interact with and swell the membrane, thereby altering initial pore characteristics and permeability. Of much greater practical importance are physical alterations of the primary gel structure to effect decreases in porosity. The most important means to this end are thermal annealing, pressurization, and solvent shrinking.

Annealing a porous membrane (particularly one which contains a nonsolvent capable of functioning to some extent as a plasticizer) results in a diminution of void volume and permeability and, because pore size is generally decreased as well, an increase in permselectivity. The reason for this can be seen on the molecular level where the introduction of thermal energy causes translational motion of the macromolecules, with the result that polar groups on the same and/or on neighboring molecules will approach one another closely enough to form virtual cross-links by dipole-dipole interactions. These cross-links tend to decrease chain mobility and, in a nonsolvent medium, are irreversible because of the inability of the nonsolvent to solvate and therefore intervene between the polar groups so enjoined.

Annealing has some effects which are continuous and some which are discontinuous. A continuous effect is the loss in water content and void volume with increasing temperature (Fig. 7.14). Water is lost from the primary gel during annealing, both because of the formation of virtual cross-links and because of the decrease in hydrogen bonding and cluster size in the water itself. An example of a discontinuous effect is the dramatic increase in permselectivity (salt retention) which is observed when cellulose acetate membranes are heated above 68.6°C, the glass transition temperature (Fig. 7.15). In fact, not one but two discontinuities are found on the permselectivity versus annealing temperature curve for cellulose acetate desalination membranes. The first signals an increase, and the second a decrease in permselectivity. The increase, on the basis of the previously cited structural

TABLE 79 DRYING TIME EFFECTS<sup>a</sup>

Drying Time (min) <sup>b</sup>	Description of Membrane	Thickness of Unheated Membrane (mm) × 10 <sup>2</sup>	Gravimetric Swelling Ratio of Unheated Membrane (wet dry/dry wt)	Rate of Water Transport (mL/cm <sup>2</sup> day) <sup>d</sup>	0.6 M NaCl Feed (%)	Salt Retention (%)
1	Opaque-opalescent (microgel blending into ultragel)	13.9	2.88	116	72	98.0
3	Opalescent (ultragel)	12.2	2.98	84	50	98.6
5	Opalescent (ultragel)	10.2	2.65	86	54	98.8
10	Opalescent-clear (ultragel)	8.5	2.41	80	50	96.3
20	Clear (ultragel)	5.8	1.75	72	50	75.1
30	Clear (ultragel)	5.3	1.60	50	36	71.5

<sup>a</sup> Kesting et al.<sup>15</sup>; © 1965.<sup>b</sup> Casting-solution composition: cellulose acetate, 22.2 g; acetone, 66.7 g; water, 10.0 g; ZnCl<sub>2</sub>, 5.0 g (doctor-blade gap, 0.25 mm).<sup>c</sup> Drying time—interval between casting at -11°C and immersion into gelation bath (0°C).<sup>d</sup> Rate of water transport and salt retention at 102 atm pressure for heated membranes (86°C for 5 min).

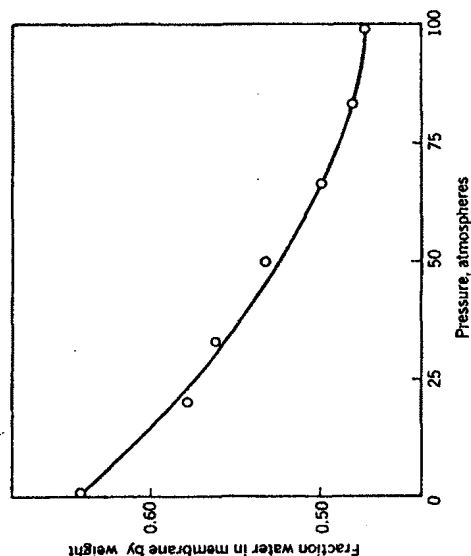


FIGURE 7.16. Membrane-water content as a function of pressure (from Kesting et al.<sup>15</sup>).

interpretation, may be attributed to the attainment of the critical interchain spacing or pore diameter, whereas the decrease may be related to disruption in the uniformity of these spacings owing to closer alignment of polymer chains in the glassy state in some regions at the expense of strain-induced removal of polymer chains from one another in others.

Whereas heating causes shrinkage in three dimensions, the application of pressure causes shrinkage primarily in one dimension, namely in the plane perpendicular to the surface. Two stages may be distinguished in the shrinkage of porous membranes under pressure (Fig. 7.16): (1) The rapid loss of void volume by the porous substructure which occurs at comparatively low pressures; and (2) the slower, more gradual loss of void volume by the comparatively dense skin layer. Inasmuch as the skin layer more closely approaches the structures of the bulk polymer, it is to be expected that significant compaction of this layer will require pressures in excess of the compressive yield point.

## 7.4 THE THERMAL PROCESS

A significant recent development in the technology of phase-inversion membranes is the invention of the thermal process by Castro.<sup>19</sup> The thermal process is applicable to a wide range of polymers, which because of their poor solubility, are otherwise inaccessible to the phase-inversion approach. In essence, the thermal process utilizes a latent solvent, that is, a substance which is a solvent at elevated (~220°C) temperatures and a nonsolvent at lower temperatures, and thermal energy to produce a Sol 1 which on cooling inverts into a Sol 2, and on further cooling gels. The reason for the incompatibility which evokes Sol 2 is loss of solvent power

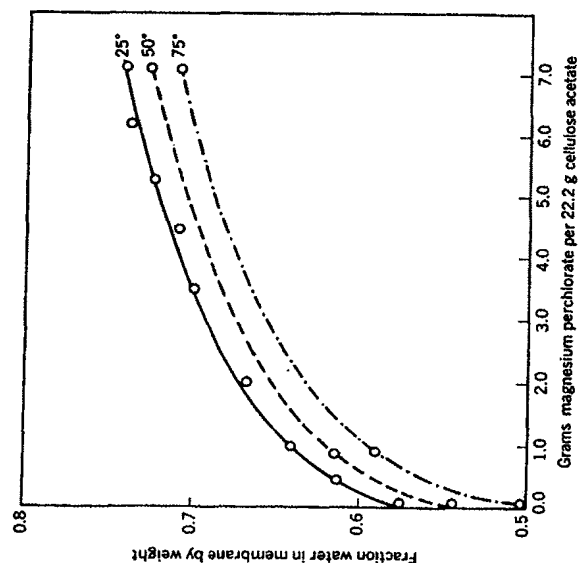


FIGURE 7.14. Membrane-water content as a function of temperature (from Kesting et al.<sup>15</sup>, © 1965).

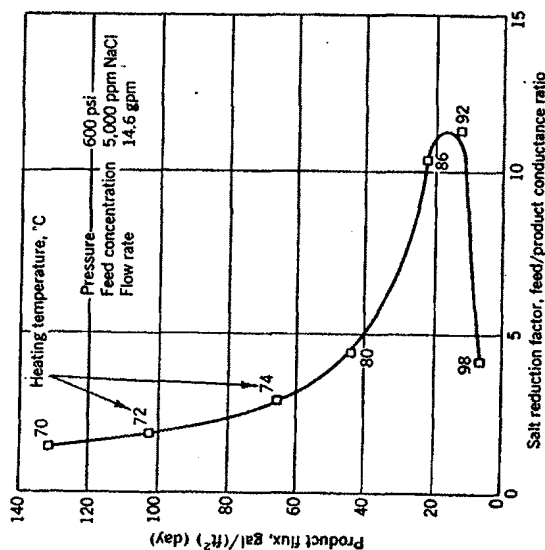


FIGURE 7.15. Permeability versus permselectivity for Loeb-Sourirajan membranes annealed at various temperatures.

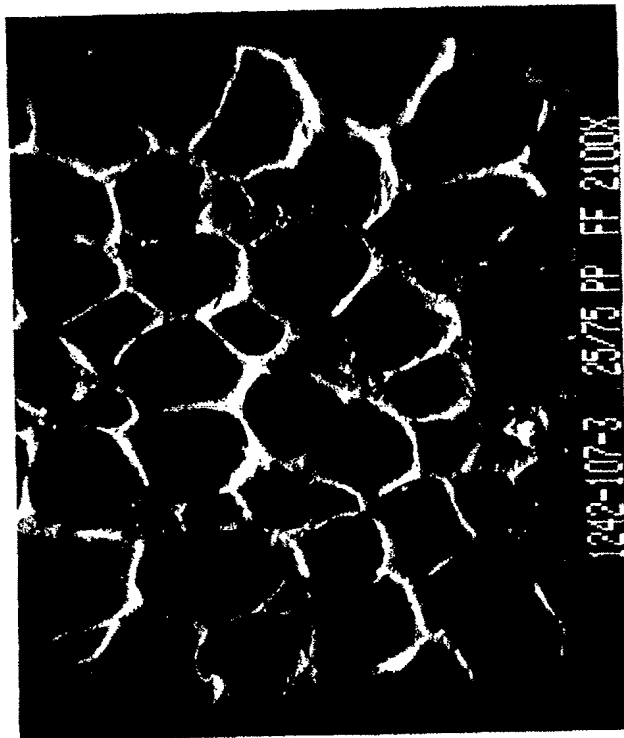
by the removal of heat. Both liquids and solids can serve as latent solvents. If, however, a solid is employed, it must be a liquid at the temperature at which Sol 2 appears. Because the latent solvents are nonvolatile substances, they are removed from the final gel by extraction with a liquid which is a solvent for the latent solvent and a nonsolvent for the polymer.

Although the thermal process is the most universally applicable of all the phase-inversion processes in that it can be utilized for the widest range of both polar and nonpolar polymers, its use for membrane applications will probably concentrate most heavily on the polyolefins, particularly on the polypropylenes. A large number of substances can function as latent solvents (Table 7.10). They usually consist of one or two hydrocarbon chains terminated by a polar hydrophilic end group. They, therefore, exhibit surface activity which may explain their ability to form the emulsionlike Sol 2 micelles at elevated temperatures. One latent solvent which is worthy of special mention because of its broad applicability is *N*-tallowdiethanolamine (TDEA). The thermal process has a number of unique features:

1. Spherical shape of the cells in the final gel matrix. Although all phase-inversion membranes possess spherical micelles in their nascent Sol 2 condition, only thermal process Sol 2 solutions retain a spherical micellar shape in the final open-cell gel structures (Fig. 7.17). The diameters of the cells lie between 1 and 10  $\mu\text{m}$  and the apertures or pores between them have diameters of between 0.1 and 1  $\mu\text{m}$  with a narrow pore-size distribution. The Sol 2 micelles of dry- and wet-process

TABLE 7.10 THERMAL PROCESS POLYMERS AND LATENT SOLVENTS<sup>a</sup>

Polymer <sup>b</sup>	Latent Solvent(s)	Extrusion Temperature (°C)
LDPE	Saturated long-chain alcohols	—
HDPE	TDEA	250
PP	TDEA	210
PS	TDEA, dichloro benzene	200
PVC	<i>trans</i> -Stilbene	190
SBB	TDEA	195
EAA	TDEA	190
Noryl (PPO/PS)	TDEA	250
ABS	1-Dodecanol	200
PMMA	1,4-Butanediol, lauric acid	210
Nylon 11	Sulfolane	198
PC	Menthol	—

<sup>a</sup>From Castio.<sup>19</sup><sup>b</sup>Commonly employed abbreviations.FIGURE 7.17. SEM photomicrograph of cross section of thermal process membrane with spherical cells (from Castro<sup>19</sup>).

membranes deform into polyhedra and flatten out by the time they have been fully formed.

2. Only the thermal process is capable of yielding isotropic microporous structures in thick sections. Wet and dry processes tend to become increasingly anisotropic as the thickness of the membrane gel is increased. This unique property renders thermal process gels suitable for use in controlled-release applications in which the gels can be cooled, ground up, extracted, and filled with, for example, volatile insect repellents.

If the solution is cooled slowly (8–1350°C/min), Sol 2 micelles appear. If, however, cooling is too rapid ( $\geq 2,000^\circ\text{C}/\text{min}$ ), a continuous lacelike noncellular polymer network is apparent in the SEM photomicrograph (Fig. 7.18). This lacelike network may represent the frozen Sol 1 structure which for kinetic reasons is unable to assume the Sol 2 configuration before it becomes immobilized.

If the solution is cooled by casting on a metal belt, the bottom surface, that is, the side adjacent to the belt, will be skinned, whereas the top surface, the side adjacent to the air-solution interface, will be skinless. This is just the opposite of what usually occurs in wet and dry processes. The skin thickness is approximately equal to the thickness of a single-cell wall and can either be integral (totally nonporous) or nonintegral (some porosity) depending on the particular conditions. The

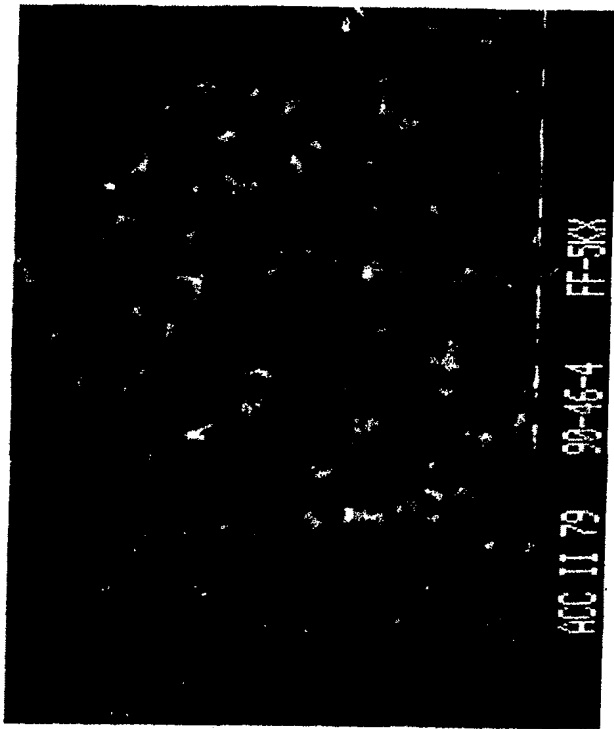


FIGURE 718. SEM photomicrograph of rapidly ( $2000^{\circ}\text{C}/\text{min}$ ) cooled 75% porosity polypropylene illustrating lacelike (possibly Sol 1) structure (from Castro<sup>19</sup>).

presence of an integral skin is desirable if the membrane is to be utilized for gas separations, HF, UF, and so on. If, on the other hand, no skin is desired it may be removed by allowing the membrane to be exposed briefly to a suitable solvent such as hexane in the case of polypropylene.

The latent solvent is removed from the membrane gel after the latter has attained sufficient strength to allow further processing. Typical leaching agents include volatile liquids such as isopropanol, methyl ethyl ketone, tetrahydrofuran, ethanol, and heptane.

## 7.5 THE POLYMER-ASSISTED PHASE-INVERSION (PAPI) PROCESS

The *polymer-assisted* variation of the phase inversion process (PAPI) utilizes a solution consisting of a solvent and two physically compatible polymers to cast a dense film with a morphology known as an interpenetrating polymer network (IPN). After complete (dry PAPI) or partial (wet PAPI) solvent evaporation, the IPN film is immersed in a liquid, usually water, which is a solvent for one of the polymers and a nonsolvent for the other. The insoluble network which remains after leaching is a skinless microporous PAPI process membrane. As originally conceived, the polymer which was to be leached was viewed as filling the role of a nonsolvent

pore former, albeit one of higher than usual MW. As such it assisted the membrane polymer to assume the Sol 2 micellar structure prior to gelation. Physical, *but not single*  $T_g$ , compatibility is required for practical PAPI blends. Too compatible a blend presumably leads to Sol 1 structures which gel as such without assuming the necessary Sol 2 configuration. PAPI membranes are usually skinless, isotropic with a narrow pore-size distribution, of intermediate porosity ( $\sim 50\%$ ), and characterized by good to excellent mechanical properties. The choice of both membrane and leaching polymers for the PAPI process is governed by the rules which are applicable to polymer blends which, unfortunately, given our present level of understanding, means that it is made on a largely empirical basis.

A potential application for PAPI process membranes is to serve as microporous supports for thin-film composites. This is particularly attractive in the *reverse sequence* (RS) method for forming defect-free thin-film composites (see Section 7.7), where the thin film can be deposited prior to leaching the assisting polymer, thereby providing a dense impermeable surface which is ideal for coating. After a thin film of preformed-, or *in situ*-, formed polymers from fluid solutions has been deposited and/or cured, the support layer of the composite membrane can be made porous by leaching.

## 7.6 INHOMOGENEITY IN DEPTH

Prior to 1960, only isotropic or slightly anisotropic phase-inversion membranes were known. Today there are two types of inhomogeneity in depth which are of importance: *skinning* and *anisotropy*.

Skinning or asymmetry refers to a structure in which a thin ( $0.1\text{--}0.25\text{ }\mu\text{m}$  in depth) dense skin layer is integrally bonded in series with a thick ( $\sim 100\text{ }\mu\text{m}$ ) porous substructure. The skin layer determines both the permeability and permselectivity of the bilayer, whereas the porous substructure functions primarily as a physical support for the skin. The first skinned membrane, the wet-process cellulose acetate type developed by Loeb and Sourirajan<sup>20</sup> in 1960 for desalination by hyperfiltration, is universally acknowledged as the instrument which heralded the advent of the golden age of membranology. In the Loeb and Sourirajan, or *integratedly-skinned*, membrane, skin and substructure are composed of the same material. Differences in density between the two layers are the result of interfacial forces and the fact that solvent loss occurs more rapidly from the air-solution and solution-nonsolvent bath interfaces than from the solution interior. Certain aspects of the skin layer remain a hotly debated issue. The earliest EM studies failed to discover any specific details of the microstructure, from which it was deduced that the skin was in an amorphous glassy state, similar to that of a solvent-cast bulk film. As we shall see, this conclusion was only partly true. Schultz and Asunmaa<sup>21</sup> discovered the presence of ( $\sim 200\text{ }\text{\AA}$  in diameter) spherical micelles in the skins of cellulose acetate membranes which had been etched with argon ions. Similar micelles were subsequently found by Kesting<sup>6</sup> in the skins of dry-process mem-

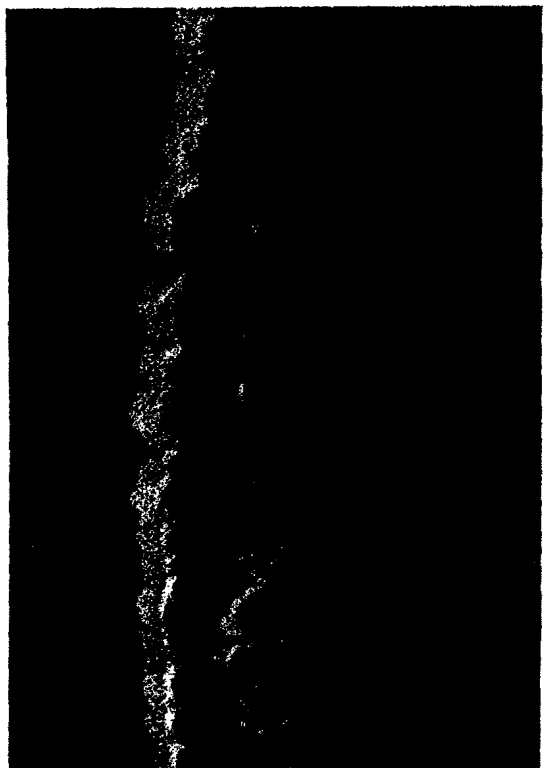


FIGURE 7.19. Top edge of cross section of polyamide-hydrazide skinned gel membrane (from Panar et al.<sup>22</sup>; reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).

branes of cellulose acetate. Panar et al.<sup>22</sup> then discovered that the micellar morphology was quite general to integrally-skinned membranes not only of cellulose acetate but of polyamide-hydrazides and polyamides as well.

In the paragraphs that follow, the findings of the classical study of Panar et al. are cited at length in their own precise and descriptive terms.

The surface structure as shown in Figure 7.19 for a polyamide-hydrazide membrane is formed from a closely packed monolayer of micelles of about 400- to 800-Å diameter. The substrate (i.e., the structure immediately below the skin or uppermost layer of micelles...) is composed of similar spherical units randomly oriented with 75- to 100-Å voids between spheres. In the surface layer these structural units are compressed and distorted so that few voids appear. The skin is thus a denser form of the same "micellar" structure which forms the bulk of the membrane.

The surface must, however, be considered as a distinct mechanical entity. During the fracture procedure, the skin is frequently separated from the bulk. In Figure 7.19 it is evident that there are more pronounced cracks between surface and the bulk than between micelles of the surface. In Figure 7.20 we see a section of surface layer free of its substrate. The grainy surface in this micrograph is the fracture surface of the water surrounding the gel membrane. The skin has been broken off the substrate during fracturing and has adhered to the water "pot." The fact that the surface layer can be separated demonstrates the relatively poor fusion of the micelles directly below the surface. The substrate is itself poorly fused and relatively spherical.

The picture of the partial fusion of the structural units in a "skinned" gel membrane requires that if the entire structure were exposed to strong surface tension forces, as



FIGURE 7.20. Surface skin of polyamide-hydrazide membrane (from Panar et al.<sup>22</sup>; reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).

in the drying of the membrane, the micelles would be expected to fuse, just as a layer of freshly applied latex paint fuses to a solid. Consistently, Figure 7.21 shows the fracture surface of dried polyamide-hydrazide gel membrane of the type discussed above. The fusion of the micelles to form a typically homogeneous, bulk phase is clearly evident.

The micellar structure of "skinned" membranes having a surface monolayer as the functional portion appears to be general. Polyamides (Fig. 7.22) and cellulose acetate (Fig. 7.23) gel membranes exhibit the same structure, as do freeze-dried polyamide-hydrazides (Fig. 7.24). The freeze-drying procedure, by obviating surface tension forces, apparently permits the micellar structure to be retained in the dry state.

The closely packed micellar morphology of the surface layer supports mechanistic hypotheses which assume permeation through free volume (dynamic pores) rather than through static pores. It seems reasonable that most permeation takes place through the anomalously high free volume in the zones between micelles when the deformed spheres are imperfectly fused.

Note, however, that these intermicellar low-density regions can themselves be considered as the static pores in Sourirajan's<sup>23</sup> model.



FIGURE 7.21. Fracture surface of air-dried polyamide-hydrazide membrane (from Panar et al.<sup>22</sup>; reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).



Areas in the surface which are imperfectly ordered, such as the gap visible in the right side of Figure 7.20 and the central region in Figure 7.23 represent defects because they occur too infrequently to be the significant morphology. These static pores would permit salt passage. The substrate presents comparatively little impedance to flow because water can move through the 100-Å gaps between the spheres.

The micellar structures of which the membranes are found appear to derive, at least for polyamide-hydrazides, from the structure of the solution from which the membrane is cast.

Note, these are the Sol 2 micelles in the present author's terminology. They are present in every phase-inversion membrane, even in those which are skinless.

The casting solution not only exhibits the same micellar structures as the bulk (Fig. 7.25) but the micelles form a surface monolayer under the influence of surface tension. Figure 7.26 is the fracture cross section of an air-liquid interface of the dimethylacetamide solution of the polyamide-hydrazides used to cast the membranes discussed above. The angle of view represented in Figure 7.26 is at 45° to the fracture cross section so that one sees the fracture surface at one side of the photograph and a section of the air interface at the other. The air interface appears structureless probably because of the effect of surface tension on the solvent. The micelles are only visible where a fracture has emphasized the mechanical differences between micelles and solvent. The micellar structure is not consistently visible on the surface of a dry *skinned* membrane, e.g. a freeze-dried gel membrane of a polyamide-hydrazide. When not visible the micellar nature can be made clear by a brief oxidative etching of the surface.

The apparent disappearance of the micellar structure was also noted by Schulz and Asunmaa<sup>21</sup> and Kesting<sup>6</sup> who employed etching with argon ions to bring the micellar structure to the fore in the skins of wet, and dry, CA membranes, respectively.

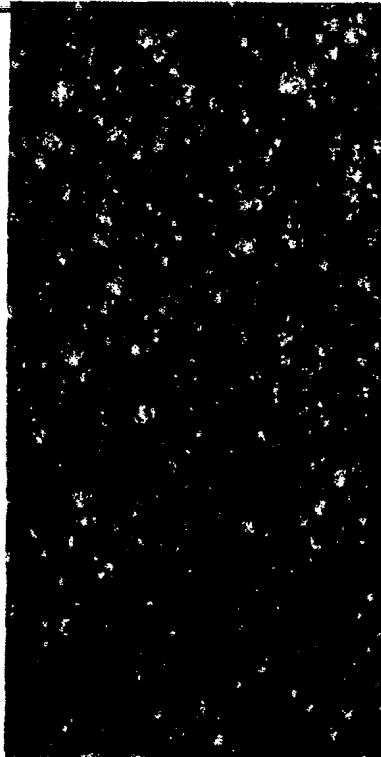


FIGURE 7.25. Fracture surface of casting solution of polyamide-hydrazide membrane (from Panar et al.<sup>22</sup>; reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).



FIGURE 7.22. Skin structure of polyamide skinned membrane (from Panar et al.<sup>22</sup>; reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).



FIGURE 7.23. Skin structure of cellulose acetate membrane (from Panar et al.<sup>22</sup>; reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).

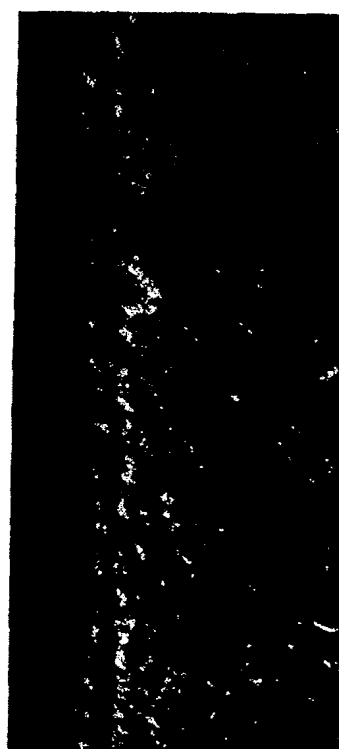


FIGURE 7.24. Skin structure of freeze-dried polyamide-hydrazide membrane (from Panar et al.<sup>22</sup>; reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).



FIGURE 726. Air-solution interface of polyamide-hydrazide casting solution (from Panar et al.<sup>22</sup>, reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).



FIGURE 727. Air-solution "skin" of polyamide-hydrazide casting solution (from Panar et al.<sup>22</sup>, reprinted with permission from *Macromolecules*, © 1973 American Chemical Society).

The brief period between forming the air interface and freezing the solution to a rigid glass (about 60 s at 25° in this case) is apparently sufficient to result in a surface layer of some mechanical integrity as can be seen in Figure 7.27 in which a section of surface layer has, during fracturing, broken free.

The rapid appearance of the surface monolayer after casting is consistent with the demonstrated importance of air exposure prior to "gelation" in determining membrane properties.

The "skinned" membrane is thus seen to be related to the structure of the freshly cast polymer solution. The various procedures devised to prepare a high flux membrane appear to have been optimized to retain the solution structure in the solid phase. One may consider this trapped solution morphology as a functional definition of the "skinned" membrane of the type first described by Loeb and Sourirajan. This viewpoint clearly differentiates such membranes which have yielded the highest reverse

osmosis fluxes from those fabricated with a thin dense layer of normal solid morphology.

The question of whether the micelles in the casting solution exist at room temperature, or form during the rapid freezing to a glass, requires comment. In the latter case, the freezing process must be considered to produce changes analogous to those occurring during "gelation," and the discussion above would refer to an undescribed solution orientation which leads to the micellar structures on freezing. The prior existence of the micelles is, however, suggested by the constancy of their sizes when a solution is frozen either very slowly or extremely rapidly in the form of a capillary film.

Immediately below the skin layer of integrally-skinned membranes is found a substrate<sup>22</sup> or transition<sup>24</sup> layer with a density intermediate between that of the skin and that of the porous substructure. This consists of less closely packed micelles than those in the skin layer and is composed of closed cells, and mixed open and closed cells. The depth and structure of the transition layer in wet-process membranes are functions of the various fabrication parameters rather than immutably fixed quantities. Although they are commonly found in wet-process membranes which employ concentrated polymer casting solutions, they are encountered in dry-process membranes, which employ more dilute casting solutions, only under specialized conditions. Trudelle and Nicolas<sup>25</sup> utilized light reflection, differential reflectometry, and densitometry and found that the skin has a water content of 38% by weight, whereas the substructure contains 61.8%. They found that the water content increases steadily from the surface inward, quite quickly in the surface region and more slowly, but not negligibly, in the deeper regions (Fig. 7.28). The transition layer was estimated to be 19  $\mu\text{m}$  (out of a total membrane thickness of 140  $\mu\text{m}$ ). Significantly, it was found that annealing the membrane resulted in increased asymmetry. The water content was decreased to a greater extent in the skin than in the substructure layer (Table 7.11).

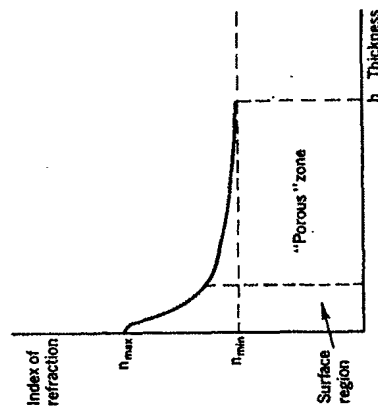


FIGURE 7.28. Variation of the index of refraction with penetration into the top surface of a Loeb-Sourirajan type of cellulose acetate membrane (from Trudelle and Nicolas<sup>25</sup>).

TABLE 7.11 EFFECT OF THERMAL ANNEALING UPON THE INDICES OF REFRACTION AND WATER CONTENTS OF SKIN AND SUBSTRUCTURE LAYERS OF LOEB-SOURIRAJAN-TYPE MEMBRANES<sup>a</sup>

Membrane	Skin Layer		Substructure Layer	
	Index of Refraction	%H <sub>2</sub> O	Index of Refraction	%H <sub>2</sub> O
N.T. <sup>b</sup>	1.409	46	1.3799	63
T. <sup>c</sup>	1.420	38.6	1.3823	61.8

<sup>a</sup>From Trudelle and Nicolas.<sup>23</sup><sup>b</sup>Unheated membrane.<sup>c</sup>Membrane heated at 80°C for 5 min.

The conclusion which can be drawn from the above studies is that the skin layer in integrally-skinned hyperfiltration membranes consists of a single layer of consolidated Sol 2-type micelles and that this structure differs in kind from that of a solvent-cast film which is the result of the direct conversion of Sol 1, a molecular dispersion of macromolecules, to the gel without the intermediate step of Sol 2 micelle formation. Thus supermolecular structure of a very specific nature is present in the skin of integrally-skinned hyperfiltration membranes which is not present either in specially prepared thin films of the type utilized by Krishnamurthy and McIntyre<sup>26</sup> to mimic the skin layer or in the thick dense films utilized by Lonsdale<sup>27</sup> to determine the "intrinsic" salt rejections of various polymer HF membrane candidates. The ultrathin film X-ray studies of Krishnamurthy and McIntyre and the thick solvent-cast film DSC (differential scanning calorimetry) studies of Morrow and Sauer<sup>28</sup> were previously cited<sup>29</sup> as evidence for the existence of crystallinity in the skin layer of integrally-skinned membranes. However, from the vantage point of our present state of knowledge of the skin structure, it now appears that these two studies were largely irrelevant since they dealt with structures which were unrelated to those of the skins in integrally-skinned membranes. Furthermore, several additional facts argue against the necessary existence of crystalline order in the skins of HF membranes:

1. Interfacial thin-film polycondensates whose mode of formation makes crystallinity highly improbable are known to function as excellent HF membranes.
2. Richter and Hoehn<sup>30</sup> deliberately designed their aromatic polyamides to be amorphous and yet they are highly permselective.
3. The trimethyl ammonium salts of CA 11-bromoundecanoate both by themselves and as blends with CA<sup>31</sup> result in integrally-skinned membranes with the highest permselectivity in a series of quaternized omega haloesters of various chain lengths. Since the inclusion of long aliphatic chains into cellulose (Table 7.12) is known to result in lower  $T_m$  values and hence in lower crystallinity, it follows that crystallinity in the skins of integrally-skinned membranes is not only unnecessary but may actually be detrimental.

TABLE 7.12 APPARENT MELTING TEMPERATURES OF VARIOUS HIGHER ALIPHATIC ACID TESTERS OF WOOD PREPARED BY THE TFAA OR THE CHLORIDE METHOD<sup>a</sup>

Sample (acyl)	N (carbon atoms)	Melting Temperature (°C)	
		TFAA	Chloride
Butyryl	4	300	310
Valeryl	5	235	305
Capryl	6	250	260
Capryloyl	8	210	245
Capryl	10	205	290
Lauryl	12	195	240
Myristoyl	14	200	—
Palmitoyl	18	195	195
Stearoyl	20	—	220

<sup>a</sup>From Shiraiishi.<sup>32</sup> Reprinted with permission from CHEMTECH, © 1983 American Chemical Society.<sup>b</sup>Measured under a pressure of 3 kg/cm<sup>2</sup>.

To accommodate both micellar skins and interfacial thin films into a single structural model consistent with the functional behavior of skins of HF membranes is quite obviously not an easy task. Since the skin is not crystalline, it is amorphous. It cannot be a rubber so it must be a glass. Since, however, the glassy state is a nonequilibrium condition, a good deal of uncertainty regarding the nature of this state and how it relates to HF membrane performance remains.

In view of the above, the "solution-diffusion" theory of demineralization by HF membranes should be critically reexamined. Consider the following:

1. The structures of the skins of integrally-skinned and thin-film composite membranes are known to be different in kind from those of the thick dense films of the type which are utilized to determine *intrinsic* salt rejections.
2. Chan et al.<sup>33</sup> have calculated that HF membranes have pores with two different pore-size distributions.
3. Katoh and Suzuki<sup>34</sup> have developed a new EM technique which has enabled them to establish the presence of pores within integrally-skinned CA HF membranes.
4. Panar et al.<sup>22</sup> have obtained EM evidence (Figs. 7.20 and 7.23) that imperfections in the form of imperfectly fused micelles exist in the skins of integrally-skinned membranes. It seems probable that these gaps represent the larger of the two pore-size distributions calculated in (2) and seen in (3) above.
5. Mathematical treatments<sup>35</sup> of various models suggest that pore defects combined with predictions from solution-diffusion theory yield the best agreement between theory and experiment. With these thoughts in mind it is time to restrict

predictions from the hyperfiltration variation of the solution-dunusion model to some specially prepared defect-free dense films which are unrelated to any functional membrane,<sup>36</sup> whether of the integrally-skinned, or of the thin-film composite, types.

Perhaps because more attention has centered on hyperfiltration membranes, the fine pores present in their skins were observed prior to their discovery in the functionally larger-pored skins of ultrafiltration (UF) membranes. Recently, however, pores of  $\sim 30$  Å have been observed by Zeman<sup>37</sup> in the skins of a UF membrane with a MW cutoff of  $10^5$  (Fig. 7.29). Their density, uniformity, and diameters leave no doubt that these are actually the pores which are functional during UF. Furthermore, since our ability to actually "see" the intermicellar defect pores (the population of larger-size pores) in the skins of HF membranes extends to the 10-Å range, it is not unreasonable to expect that at some point we shall be able to extend this ability to the population of smaller-sized pores, whose existence is predicted by Sourirajan's pore theory.<sup>23</sup>

The list of polymer membrane materials is virtually endless insofar as possible chemical varieties are concerned. However, the number of fundamental physical structures into which they may be formed is much more limited. For present purposes, a distinction is made between skinned membranes and skinless ones. However, in view of the substantial and growing evidence cited above for the existence of pores in HF and UF membranes, even this is done with trepidation. Further subdivision results in three types of skinned membrane: (1) integrally-skinned ultragels; (2) integrally-skinned microgels; and (3) nonintegrally-skinned microgels, the thin-film composite membranes. Such skinned membranes are utilized in gas



FIGURE 7.29. SEM micrograph ( $\times 10^5$ ) of polysulfone UF membrane with MW cutoff 100,000 (from Zeman<sup>37</sup>).

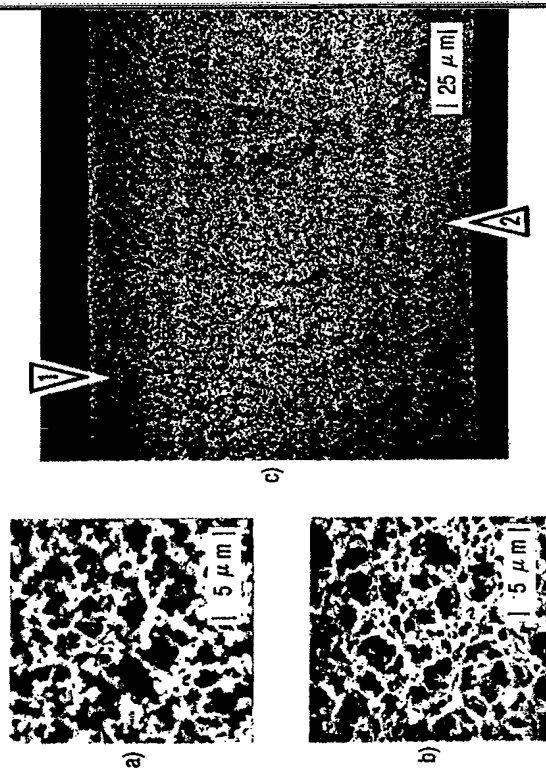


FIGURE 7.30. SEM micrograph of an isotropic 0.45- $\mu$ m membrane: (a) surface at 1; (b) surface at 2; (c) cross section (from Kesting et al.<sup>7</sup>).

separations, hyperfiltration, and ultrafiltration. On the other hand, two types of skinless membranes are discernible and both are utilized in microfiltration and related applications: (1) isotropic (actually, slightly anisotropic) microgels and (2) highly anisotropic microgels.<sup>38</sup> The former are the conventional microfiltration membranes of commerce. Both surfaces of the conventional membrane are quite similar in appearance (Fig. 7.30a,b) and the cross section (Fig. 7.30c) reveals only a slight degree of anisotropy with little difference in pore and cell size from one surface to the other. In contrast, a considerable difference is apparent between the pore sizes at opposite surfaces of the highly anisotropic microgel (Fig. 7.31a,b). SEM photomicrographs reveal a degree of anisotropy (DA), that is, a difference in pore size from one surface to the other, of approximately 5. The cross section indicates the presence of two integral layers, the thicker of which contains the coarser cells (Fig. 7.31c).

A simple but graphic illustration of the morphology of anisotropy is also afforded by a wick test. In this procedure, a hollow-point pen is brought into contact with either surface of (in this instance) a 0.45- $\mu$ m microfiltration membrane. Circular ink stains of unequal diameter then appear on opposite sides of the filter. Photomicrographs of the cross sections of the stained membranes indicate wicking patterns attributable to differences in capillarity. A low degree of anisotropy leads to minimal wicking (Fig. 7.32a); an intermediate degree of anisotropy to modes wicking (Fig. 7.32b); and a high degree of anisotropy to maximum wicking (Fig. 7.32c). In the last of these an integral bilayer is indicated, one part consisting of

fine cells (in which capillarity is quite pronounced) and the other of much coarser cells (Fig. 7.32d).

This gradation of pore sizes from one surface to the other confers the filtration capacity of a prefilter-filter combination upon these integral bilayers and accounts for their significantly higher dirt-holding capacity. Because the fine-pored layer of highly anisotropic membranes is only a fraction of the overall membrane thickness, its cells and pores are deliberately made smaller than those of a similarly rated isotropic membrane filter. For example, a 0.2- $\mu\text{m}$ -rated highly anisotropic membrane may have pores in its fine layer of  $\sim 0.15\ \mu\text{m}$  or even  $0.1\ \mu\text{m}$  and pores in its coarse layer as large as  $10\ \mu\text{m}$ . In the latter case the DA equals 100.

Highly anisotropic membranes are produced by manipulation of casting-solution parameters such as solvent volatility and environmental factors such as temperature and relative humidity which influence the kinetics of phase inversion, gelation, syneresis, and capillary depletion. The surface of the membrane which constitutes the air-solution interface during its nascent phases becomes the fine-pored side of the finished membrane. During filtration, however, it is the coarse-pored side of the membrane which is positioned to face the feed solution. When this is done, the throughput of the highly anisotropic membrane is much greater than that of the conventional isotropic type (Fig. 2.21). The throughput is greatly diminished, however, when the fine-pored surface faces the feed, although it is still roughly equivalent to that for the coarser-pored surface of the conventional membrane.

## 7.7 COMPOSITE MEMBRANES

The combination of two or more membranes in series results in a composite membrane. The permeability constant  $P$  for a composite membrane may be expressed<sup>39</sup>

$$\frac{1}{P} = \sum_{i=1}^n \frac{x_i}{l} \frac{1}{P_i}$$

where  $P$  = overall permeability constant,

$n$  = number of layers of membrane, each of thickness  $x_i$ , and

$l$  = total thickness of the composite structure.

The permeability constant of the composite membrane is therefore represented by the harmonic average of the permeability constant of the individual layers, the respective weights being  $x_i/l$ , the ratio of layer thickness to the total. Although composite membranes include layers of dense films or even liquid layers in series with films, in this case the term is being limited to those series, at least one of whose members is a phase-inversion membrane which itself can be either of the integrally-skinned or of the skinless variety.

In the case of composite membranes consisting of skinless porous substrates and dense films, permeability and permselectivity may be determined solely by the resistance of the dense films. Different membrane polymers may therefore be employed for the thin barrier layer and the thick support structures which thereby

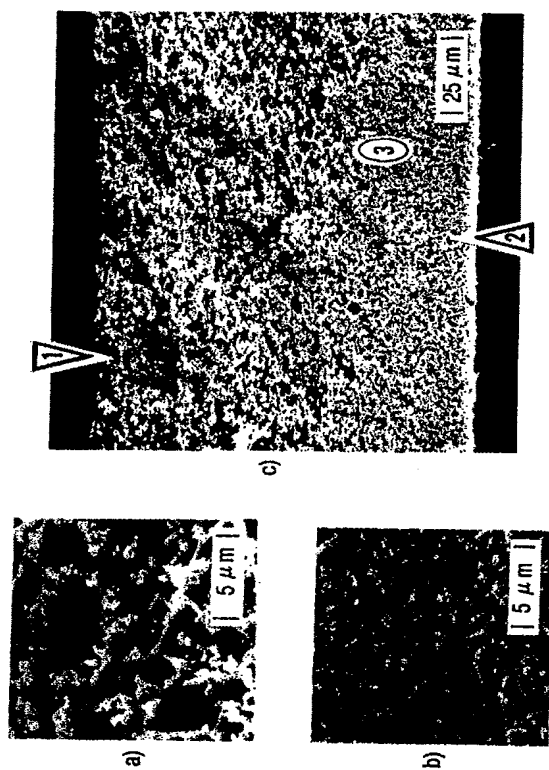


FIGURE 7.31. SEM photomicrographs of a 0.45- $\mu\text{m}$  highly anisotropic membrane: (a) surface at 1; (b) surface at 2; and (c) cross section (from Kesting et al.<sup>7</sup>).

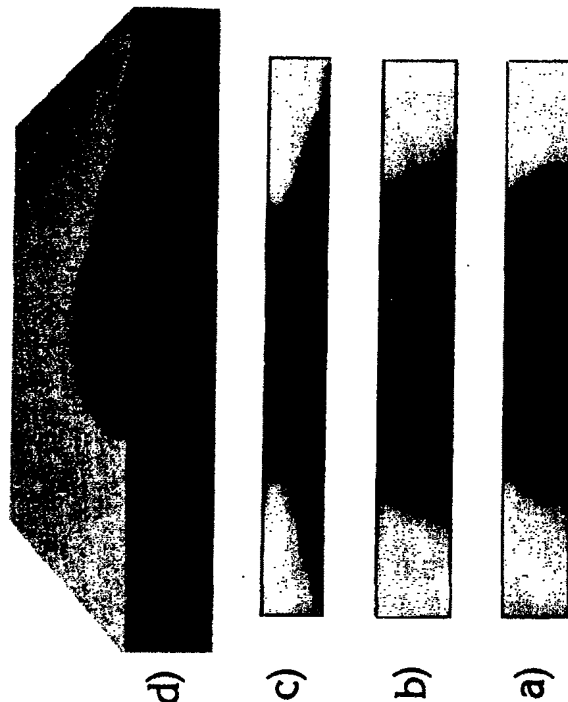


FIGURE 7.32. Photomicrographs of ink-stained cross sections of 0.45- $\mu\text{m}$  membranes with various degrees of anisotropy: (a) low DA; (b) intermediate DA; (c) high DA; and (d) artist's conception of (c) (from Kesting et al.<sup>7</sup>).

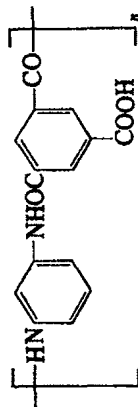
permits the attainment of a combination of properties which are not available in a single material. Such membranes were initially developed for desalination by hydropiltration where they are known as thin-, or ultrathin-, film composites or non-integrally skinned membranes. The other type of composite membrane is utilized for gas separations. It is a composite consisting of an integrally-skinned or asymmetric membrane, the defects of whose skin layer are coated by the addition of a second, albeit more permeable, skin. The inventors of the latter have entitled their device "resistance-model" membranes.

In the standard sequence for the formation of thin-film composites, a preexisting microporous membrane is utilized as a support onto which a thin barrier-layer film is deposited. It is hoped that the nature and preparation of the microporous support layer is sufficiently familiar to the reader by this time that little more need be said other than that it is a skinless microgel with approximately 0.1- $\mu$ m pores and today in most cases consists of polysulfone.

The microporous support layer can be combined with the thin film to form the thin-film composite membrane in a variety of ways:

1. A dilute solution of a preformed polymer can be separately cast, preferably from a surface-active "spreading" solvent such as cyclohexanone, onto water, thereby yielding a thin film which is then laminated to the porous support layer. This approach was originally developed by Carnell and Cassidy<sup>41</sup> and was the first one utilized by Francis and Cadotte<sup>41</sup> in 1964 to coat microporous CA membranes. Petersen<sup>42</sup> also utilized this approach to cast thin films of ethyl cellulose perfluorobutylate which were then laminated to Celgard® and Tyvek® supports for use as blood oxygenation membranes.
2. Application of either a preformed polymer or a prepolymer solution by dip coating, wicking, or some other transfer procedure directly onto the porous support where it is subsequently dried or cured. This procedure has the advantage that the difficult handling of thin films is avoided. It has the disadvantage that only solutions which do not interact with the porous support may be utilized in the application of the barrier layer. This is, of course, not a disadvantage if, as is frequently the case, the coating can be applied from an aqueous solution. This approach was first utilized by Cadotte in the application of an aqueous solution of polyethyleneimine (PEI) and the subsequent reaction with tolylene diisocyanate (TDI) in hexane to yield the cross-linked polyurea which constituted the NS-100 membrane. When PEI or an ethoxylated derivative of PEI were coated and reacted with a hexane solution of isophthaloyl chloride, the resultant thin film was a polyamide (NS-101 or PA-300). The reaction of furfuryl alcohol with sulfuric acid resulted in a sulfonated polyfuran known as NS-200. Recently, interest in coating and subsequent cross-linking of a water-soluble sulfonated polysulfone has been revived.
3. Plasma polymerization involves the buildup of a dense layer from the deposition of monomers produced in an RF plasma.<sup>43</sup> Such monomers are unrelated to those encountered in free radical polymerization. Hydrophilic coatings can sometimes be produced from materials which, prior to their conversion to a plasma, were hydrophobic and vice versa. No commercial use is being made of this approach at present.

4. Interfacial polycondensation of reactive monomers on the surface of the porous support. The basic interfacial polycondensation technique is known<sup>44</sup> to have a number of unusual but desirable features among which the lack of strict requirements for monomer purity and reagent stoichiometry are perhaps the most outstanding. Cadotte<sup>45</sup> has applied this concept to the preparation of the commercially successful FT-30 desalination membrane. A polysulfone support is coated with an aqueous solution containing at least 0.01% of *m*-phenylene diamine. The coated membrane is then brought into contact with a hexane solution containing trimesoylchloride. Reaction is swift and terminates when the completed interfacial thin film inhibits further reaction. Only slightly more than two of every three carboxylic acid chloride groups condense so that the lightly cross-linked final membrane polymer closely approximates the formula



The high permeability of the FT-30 membrane is attributable to the presence of the hydrophilic carboxyl groups. An SEM photomicrograph of the cross section shows that the barrier layer is itself composed of several layers of varying density to a total depth of approximately 0.25  $\mu$ m (Fig. 7.33). This thickness adds physical strength in the form of flexibility and abrasion resistance which earlier and thinner thin-film barrier layers did not possess. The fact that none of the thin-film composites, including FT-30, exhibits any appreciable resistance to oxidative degradation by chlorine is believed to be coincidental with the chemical characteristics of the particular thin films which have thus far been investigated rather than with the nature of thin-film composites per se. The cross-linked polyether<sup>46</sup> membrane for example, is so subject to degradation even by dissolved oxygen, that the feed must be continuously dosed with sodium bisulfite. On the other hand, thin-film composites consisting of cross-linked thin films of sulfonated polysulfone are expected to be chlorine resistant.

The finer the particles in a mixture the more difficult it is to obtain an appreciable difference in the rates at which they permeate a membrane. Thus separation of bacteria from a suspension is routinely achieved with log reduction values

$$(\log_{10} \text{ colony-forming units (CFUs) in feed}) \\ (\text{CFUs in product})$$

of between 7 and 11, whereas in HF salt reduction factors

$$\text{SRF} = \frac{\text{salt concentration in feed}}{\text{salt concentration in product}}$$

5. The *reverse-sequence* (RS) method of forming thin-film composites is an approach which, in its more common manifestation, involves the preparation of defect-free thin films in series with thick dense (but potentially porous) films. The conversion of what amounts to a thin dense film: thick dense-film bilayer to a thin film: microporous membrane composite is effected by the immersion of the bilayer into a bath where certain constituents are leached from the thick dense-film portion of the bilayer, while leaving the thin dense film intact. The result is a thin-film composite in which the preparation of the thin film preceded the preparation of, or at least the development of porosity in, the microporous layer. In the standard sequence, the microporous membrane is prepared first and then subsequently coated with a thin dense film. The latter procedure leads to defects in the thin film because of the presence of occasional large pores in the surface of the microporous substrate. In contrast the casting substrate utilized in the RS method is a smooth nonporous surface which is amenable to the preparation of defect-free thin films. In another variation of the RS method, a thin dense film is cast on a smooth nonporous surface such as glass or polished stainless steel and a microporous membrane or potentially microporous thick film is then cast onto the thin film. The composite is then released from the casting substrate by immersion in water.

## 7.8 STRUCTURAL IRREGULARITIES

A by no means exhaustive list of commonly encountered structural irregularities in phase-inversion membranes includes: irregular gelation, wavemarks, macrovoids, and blushing.

Irregular gelation can take many forms. Streaks or draglines appear at the top side of the membrane, that is, at that surface which constitutes the air-solution interface during the early nascent phases of membrane formation. If a solution is close to the point of incipient gelation when it passes under the casting knife as it is first exposed to air, virtually any imperfection, such as a scratch on the blade surface, can serve to nucleate a gel particle. This particle can adhere to the blade and cause the formation of streaks when additional gel particles are nucleated in the solution as it passes under the original site. Such premature gelation is prevented by elimination of nucleation sites by, for example, polishing the casting blade, and by postponing gelation until the solution is a safe distance downstream from the casting blade. The latter is usually accomplished by the installation of a *quiet zone* immediately downstream from the hopper. An impermeable plate, a few centimeters in length, is positioned close to the surface of the casting solution to maintain the concentration of solvent vapor at a sufficiently high enough level as to prevent gelation until the solution has passed underneath the plate. Another type of irregular gelation is visible as subsurface imperfections which are most easily seen by light-box inspection. Although such subsurface gel particles are often only a cosmetic defect, they can at times be more serious and do represent a potential locus of failure as, for example, when roll stock is convoluted for inclusion in

of 100 or less, that is, LRVs of  $\sim 2$ , are the norm. In the case of many gas separations, even lower separation factors are observed. Furthermore, because the fluidity of gases is so high, the rate of gas permeation of unseparated gas mixtures through porous imperfections in the skin layer of an integrally-skinned membrane can be so great as to overwhelm by dilution of separated gas with unseparated gas mixture, the effects of whatever separation was achieved. Thus even CA/CTA blend membranes which are capable of SRFs of 100 in a desalination application, frequently encounter difficulty when utilized, after suitable drying, as gas-separation membranes. Henis and Tripodi<sup>47</sup> noticed this effect while investigating integrally-skinned hollow-fiber membranes of polysulfone and solved the problem by applying a coat of silicone and/or other elastomers to effectively seal any imperfections in the skinned polysulfone membrane against a high flow rate of unseparated feed gas mixture. This approach should be applicable to virtually any skinned membrane. The sealing polymer coat need not itself be capable of separating gaseous mixtures so long as it is sufficiently permeable as not to significantly reduce the permeability of gases through the separating membrane, while at the same time sufficiently impermeable as to constitute a barrier to the bulk flow of unseparated gases.

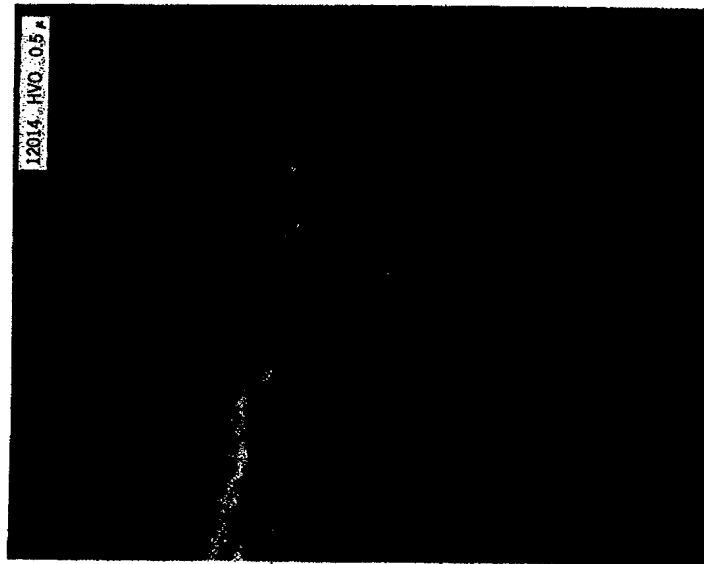


FIGURE 7.33. SEM micrograph of cross section of FT-30 membrane (from Cadotte<sup>45</sup>).

pleated cartridges. Such subsurface gels are usually attributable to inadequate filtration of the casting solution. Good manufacturing practice requires that a casting solution be constantly recirculated through a filter after it has been mixed. It then receives a final filtration just prior to its being fed into the casting hopper. Any particle, however minute, represents a potential nucleation site for random gelation. This can sometimes be seen as in the form of irregular snowflake patterns during capillary depletion. Ordinarily, snowflake patterns appear in an even line in the transverse direction across the entire width of the membrane. If they appear on one side earlier than on the other, the membrane is thinner in that area. If snowflakes suddenly appear randomly where no others are found, this may indicate a thin spot or even a pinhole. Both defects are apparent on light-box inspection.

As the name implies, wavemarks are encountered only in wet-process membranes. The casting solution enters the nonsolvent bath at which point a skin is formed as the solution is immersed. Interfacial tension causes the water to adhere to the leading edge of the membrane until continued motion of the nascent membrane into the nonsolvent medium causes the water to break away and establish another leading edge. Wavemarks represent a thickening of the membrane at the crest of the wave and, depending on various factors such as casting solution fluidity, can achieve varying amplitudes at the crests. The problem is overcome by adjusting the angle of entry of the casting solution into the nonsolvent bath.

Large (10–100  $\mu\text{m}$  in the longest dimension) subsurface voids, tear dropped, spherical, ellipsoidal, or fingerlike in shape, are known as *macrovoids*. They represent, at the very least, weak spots within the gel matrix, and at worst, that is, when located near the high-pressure surface of the membrane in pressure-driven applications, areas of potential rupture. It was once thought that fingerlike cavities represented volume elements of low resistance which contributed to overall permeability. Such cavities are never advantageous and should always be avoided whenever possible. There are two basic reasons for the appearance of macrovoids and an examination of SEM photomicrographs of membrane cross section usually permits the responsible cause to be established. When the walls of the cavity are made up of open cells which are identical to the structure of the undisturbed gel matrix, then the cavities are the effect of trapped pockets of solvent vapor which has built up in subsurface domains faster than it can diffuse out. If the surrounding matrix gels before the solvent vapor can depart, then a skinless cavity wall remains. The presence of a high concentration of solvent prevents the skinning of the cavity walls. Such voids can be eliminated by minimizing the buildup of solvent vapor by lowering solution viscosity and/or by lowering the environmental temperatures. Another cause of similar voids is the physical entrapment of air bubbles owing to leaks into the hopper area or to too rapid influx of casting solution into the hopper.

When the cavity walls are skinned, this is a clear indication that nonsolvent intrusion from the gelation bath has taken place. Such intrusions can occur irregularly when certain voids close to the surface rupture for any reason prior to the gelation of the matrix surrounding the void. Thus a given membrane can contain voids with skinned—as well as voids with skinless—interior surfaces. The fingerlike cavities, on the other hand, appear on a regular basis with predominantly

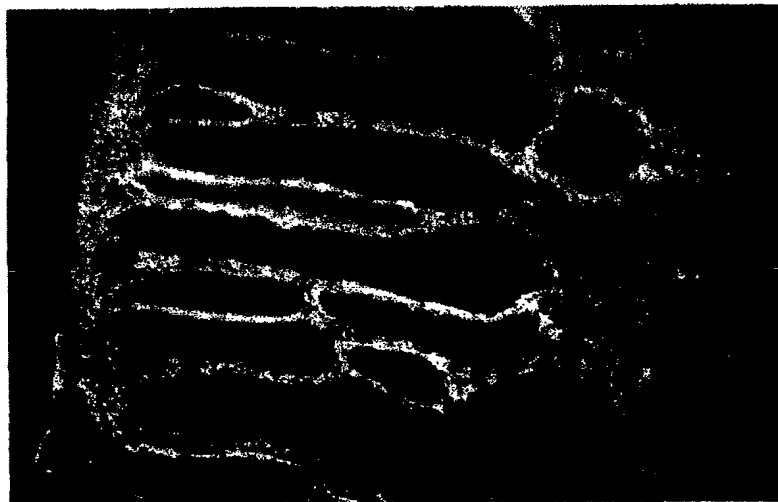
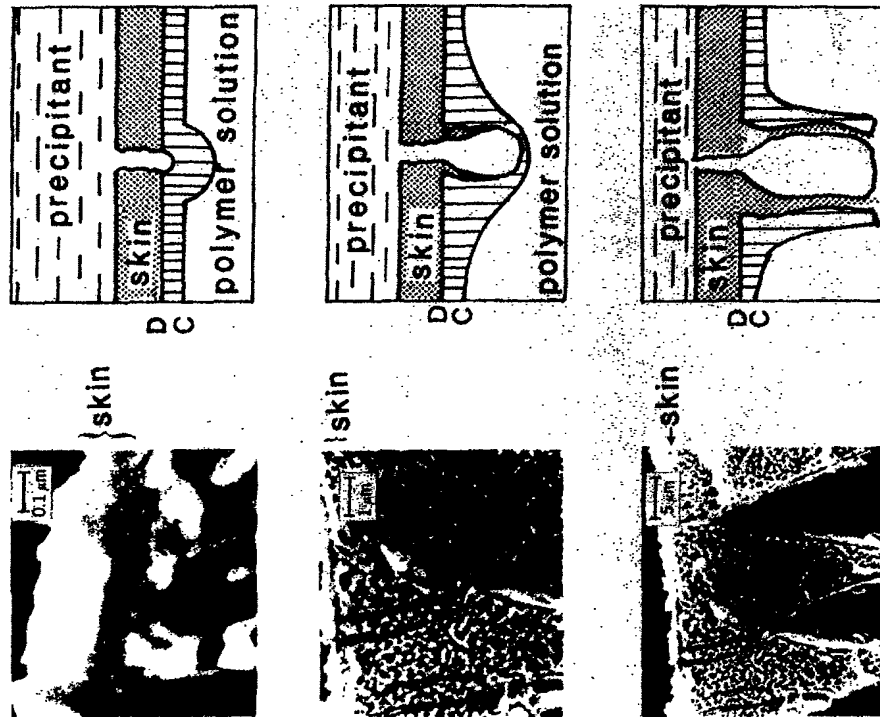


FIGURE 7.34. SEM photomicrograph of cross section of membrane with skinned fingerlike cavities. Arrows denote actual permeation pathways (from Cabasso<sup>11</sup>).

skinned interior surfaces. Cabasso has shown that no permeation of product takes place through these cavities which therefore represent useless dead space (Fig. 7.34). They appear to be due to skinning of somewhat too-fluid solutions followed by “osmotic shock” to the formed skin, which subsequently ruptures, permitting the rapid intrusion of water into the still-fluid substructure where gelation eventually takes place in the matrix surrounding the fingerlike intrusions of water (Fig. 7.35). The surface pores which result from the rupture of the skin remain, and are the reason why such UF membranes are unable to quantitatively remove bacteria whereas nominally coarser MF membranes can. They can be avoided, or at least minimized, by the addition of solvent to the gelation medium to lessen the osmotic shock and by utilizing more viscous casting solutions.

The presence of a fine white powder on one or both surfaces of a polymer film or membrane following wet or dry casting is known as *blushing*. Microscopical examination shows that the powder consists of spherical particles characteristic of polymer lattices. Obviously, the presence of these particles is, or can be, deleter-



FIGURE 7.35. Formation of fingerlike cavities (from Strathmann<sup>10</sup>).

ous because the potential exists for their inadvertent sloughing off and addition to the product stream, the purification of which was the principal reason for utilizing a supposedly integral membrane in the first place. These particles consist of the most soluble polymer components within the casting solution which is utilized in the preparation of the membrane or film. They are the constituents which remained in solution the longest which in turn means that they are soluble in the solvent system even after it has become depleted of most of the more volatile true-solvent constituents. Furthermore, it is likely that they consist of lower-MW fragments since the latter are more soluble than are those of higher MW.

Water is, in most instances, a strong nonsolvent because of which it is a causative factor in the occurrence of blushing. After phase inversion and gelation and prior to capillary depletion, the membrane gel is still filled primarily with the less

volatile nonsolvent components of the casting solution. Only residual amounts of true solvent remain. Therefore, any polymer remaining in solution is in a metastable state. The presence of water either in the solution or in the atmosphere acts to precipitate the remaining polymer. Blushing can appear at either or both surfaces. When it appears on the surface which is exposed to air during drying, it is the result of pore former (nonsolvent) liquid which has been expressed through the surface in the gel contraction known as syneresis. The expressed liquid contains the last traces of polymer in solution. Their precipitation as latex particles at this point depends on relative humidity and the composition of the syneresed liquid. The presence of blushing on the bottom surface, on the other hand, depends on the composition of the liquid which is still within the gel near the bottom surface.

There are several ways to prevent or minimize blushing:

1. Addition of a high-boiling (retarder) solvent to the mix. This is the approach taken for polymer films. It must be utilized judiciously for membranes because it can lead to loss of porosity. The presence of a solvent as the last liquid component to leave the scene prevents precipitation.
2. Elimination of water from the casting solution and/or reduction of relative humidity.
3. Employment of pore formers such as 1-butanol, which carry the water with them as they evaporate.

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## 8 OTHER POROUS MEMBRANES

Virtually all polymeric membranes, even the relatively dense types, contain some porosity or void volume. However, it is usually not until the porosity becomes comparable to the volume occupied by the polymer, so that microvoids interconnect, that the resultant membranes are considered porous. The prototype of porous membranes is, of course, the phase-inversion membrane which was encountered in Chapter 7. However, where the high porosity which is presently attainable only by phase-inversion techniques is not required, a number of viable alternatives exist.

### 8.1 SWOLLEN DENSE FILMS

The total immersion of dense membranes into a swelling system followed by exchange of this system for a nonsolvent medium is one method for the production of porous membranes. Brown<sup>1</sup> originated this swelling technique to prepare reproducible collodion membranes for biological separations. The method consists of the preparation of dense films by the air drying of nitrocellulose solutions to completion. The dense films are then immersed in solutions of ethanol and water. After subsequent washing with water, the resultant membranes exhibit permeabilities which are directly proportional to the concentration of alcohol, that is, to the solvent strength of the swelling medium. The swelling parameters representative of collodion membranes prepared by this method are found in Table 8.1.

Even a cursory glance at Table 8.1 suffices to indicate that this method is not without its limitations. The swelling ratio, which is relatively insensitive to alcohol concentration up to 90% suddenly becomes extremely sensitive at values above that. The loss of polymer substrate owing to the solvent action of the swelling medium also becomes appreciable at higher concentrations. Complications may